PB82-234311

Quality Assurance in Support of Energy Related Monitoring Activities

Rockwell International
Newbury Park, CA

Prepared for

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Apr 82

U.S. Department of Commerce
National Technical Information Service
NTIS

PB82-234311

EPA 600/4-82-037
April 1982

QUALITY ASSURANCE IN SUPPORT OF ENERGY RELATED MONITORING ACTIVITIES

Final Report

by

Mark Cher and Miriam Lev-On

Rockwell International
Environmental & Energy Systems Division
Environmental Monitoring & Services Center
Newbury Park, California 91320

Contract No. 68-02-2412

Project Officer

Steven M. Bromberg
Quality Assurance Division
Environmental Monitoring and Systems Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL MONITORING AND SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/4-82-037	ORD Report	PB82 234311

4. TITLE AND SUBTITLE	5. REPORT DATE
Quality Assurance in Support of Energy Related Monitoring Activities Final Report	April 1982
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Miriam Lev-on Mark Cher	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Rockwell International 2421 W. Hillcrest Drive Newbury Park, CA 91320	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Office of Research and Development U.S. Environmental Protection Agency	14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This summary describes and summarizes the activities and achievements of the program entitled Quality Assurance in Support of Energy Related Activities. The activities reported cover the period from July 13, 1976 to December 31, 1980.

The purpose of this program was to establish a quality assurance program to provide a data base for ambient air monitoring in specified geographical areas around present and proposed energy development projects (83), and to provide technical assistance to enable existing monitoring networks to achieve a high level of data quality. A major goal of the program was to give the U.S. Environmental Protection Agency (EPA) access to monitoring data from diverse sources for future study and planning purposes. This goal involved providing information concerning data quality from the individual monitoring networks.

The scope of work was divided into four task areas involving: (a) Quality Assurance System Audits, (b) Quality Control Reference Sample Audits, (c) Calibration Performance Audits, and (d) Technical Assistance to the Laboratories.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	76
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

This report has been reviewed by the Environmental Monitoring and Systems Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

This report describes and summarizes the activities and achievements of Rockwell International's Environmental Monitoring & Services Center (EMSC) during the four and a half years of the program entitled, Quality Assurance in Support of Energy Related Activities. The activities reported cover the period from July 13, 1976 to December 31, 1980.

The purpose of the program was to establish a quality assurance data base for ambient air monitoring in specified geographical areas around present and proposed energy development projects, and to provide technical assistance to enable existing monitoring networks to achieve a high level of data quality. A major goal of the program was to give the U.S. Environmental Protection Agency (EPA) access to monitoring data from diverse sources for future study and planning purposes. This goal involved providing information concerning data quality from the individual monitoring networks. In the West the energy projects were located in the states of Montana, South Dakota, North Dakota, Wyoming, Utah, Colorado, Arizona, Nevada, New Mexico, and California. In the East the energy projects were located in Virginia, Ohio, Pennsylvania, and Indiana. Additional organizations not directly involved in energy development projects were located in Delaware, Maryland, Virginia, and the District of Columbia.

The scope of work was divided into four task areas involving:

a. Quality Assurance System Audits - an initial on-site review of laboratories and field sites.

b. Quality Control Reference Sample Audits - a sample submissions audit program to the laboratories.

c. Calibration Performance Audits - on-site field calibration audits.

d. Technical assistance to the laboratories.

A separate task involved conducting system audits of sixteen water quality field stations operated by the U.S. Geological Survey (USGS).

A total of 36 laboratories and associated field sites were visited, inspected, and evaluated. Three of the laboratories in EPA Region VIII were visited twice. The findings were summarized in detailed system audit reports submitted to EPA. These reports included recommendations for improving performance and data quality. Similar system audit reports were submitted concerning the 16 USGS water quality field stations.

Regularly scheduled Quality Control Reference Sample Audits were conducted for the analysis of sulfate ($SO_4^=$), nitrate (NO_3^-), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), and carbon monoxide (CO), and for weight measurement and high-volume flow rate. In these surveys reference samples or devices were submitted to participating laboratories and their results compared with those obtained by Rockwell.

Performance results for all chemical analyses exhibited steady improvement over four years of quarterly audits. The results for NO_2 and CO were noteworthy for consistently high quality, especially CO.

Weighing performance has been quite satisfactory. A few agencies which did not meet a target level of performance were able to trace weighing difficulties to faulty balance adjustment. The high volume audits showed notable improvement in the ability of agencies in correctly calibrating flow rates.

Over 420 performance audits at the field stations were conducted to check for calibration accuracy of continuous analyzers. In these audits, known concentrations of pollutants are delivered to each continuous analyzer, and the observed response is compared with that predicted by the agency's calibration. Procedures have been developed to assure reliable performance by the audit devices and standards. Additional checks on the equipment and procedures are made by means of quarterly audits performed at EPA's Environmental Monitoring and Systems Laboratory at Research Triangle Park, North Carolina.

A major achievement of the program has been the marked improvement in the calibration accuracy observed for several pollutants, especially nitric oxide, nitrogen dioxide, nitrogen oxides, and ozone. Calibration accuracy for CO has been shown to be quite good from the beginning of the program.

In addition to audit activities, technical assistance has been provided to participating agencies as requested by the Project Officer. Much of this assistance was given informally during site visits. During the special visit by Rockwell personnel, assistance was also provided concerning specific laboratory and calibration procedures. The major technical assistance areas were in air monitoring procedures and quality assurance, chemical analysis and quality control procedures, trace metal analysis, traceability to NBS, special audits, and guidelines reviews.

This report is submitted in fullfillment of Contract No. 68-02-2412 by Rockwell International's Environmental Monitoring & Services Center under the sponsorship of the U.S. Environmental Protection Agency.

CONTENTS

Abstract iii
Figures vi
Tables vii

1. Introduction 1
2. Summary and Conclusions 3
3. Quality Assurance System Audits 4
    Air monitoring programs 4
    U.S. Geological Survey Field Stations 11
4. Quality Control Reference Sample Audits 13
    Introduction 13
    Sulfate/Nitrate analysis 15
    Sulfur Dioxide 18
    Nitrogen dioxide analysis 22
    Carbon Monoxide analysis 28
    Weighing survey 31
    High-volume flow rate calibration audits 31
5. Performance Audits 36
    Evaluation criteria 47
    Audit results 49
6. Technical Assistance 54
    Technical assistance areas 54

References 59
Appendix 60

A. Description of audit procedures and evaluation criteria . . . 60

FIGURES

Number		Page
1	Histograms illustrating improvement in high-volume flow rate calibration performance	35
2	Average calibration error as a function of time for NO, NO_x, NO_2 and O_3	51
3	Average calibration error as a function of time for SO_2 CO, and CH_4/THC	52

TABLES

Number		Page
1	Summary of Quality Assurance System Audits Performed in The Western QA Program	5
2	Summary of Quality System Audits Performed in the Eastern QA Program	8
3	Typical System Audit Summary List of Recommendations	9
4	Summary of the USGS Laboratories Surveyed	12
5	List of Participants in the Interlaboratory Performance Survey for $SO_4^=/NO_3^-$	16
6	Composite Performance for $SO_4^=$ Audits	17
7	Composite Performance for NO_3^- Audits	18
8	Summary of Agency Performance for $SO_4^=$ Analysis	19
9	Summary of Agency Performance for Analysis of NO_3^-	20
10	List of Participants in the Interlaboratory Performance for SO_2	21
11	Composite Performance for SO_2 Audits	22
12	Summary of Agency Performance for SO_2 Analysis	23
13	List of Participants in the Interlaboratory Performance Survey for NO_2	24
14	Composite Performance for NO_2 Audits	25
15	Summary of Agency Performance Analysis of NO_2	26
16	List of Participants in the Interlaboratory Performance Survey for CO	27
17	Composite Performance for CO Analysis	28
18	Summary of Agency Performance for Analysis of CO	29
19	List of Participants in the Performance Audits Weighing and Hi-Vol Flow Calibration	30
20	Summary of Agency Performance for Weighing Audit	32
21	Summary of High Volume Flow Rate Audits	34
22	Summary of Audits Performed by Rockwell in 1976	36
23	Summary of Audits Performed by Rockwell in 1977	37
24	Summary of Audits Performed by Rockwell in 1978	39
25	Summary of Audits Performed by Rockwell in 1979	42
26	Summary of Audits Performed by Rockwell in 1980	46
27	Summary of Audit Results	50
A-1	Calibrator Operational Check	64

SECTION 1

INTRODUCTION

This report summarizes the activities of Rockwell International Environmental Monitoring and Services Center (EMSC) pursuant to Contract No. 6801-2412, entitled Quality Assurance In Support of Energy Related Monitoring Activities. This program was initiated on July 13, 1976, and work continued till December 31, 1980, a period of about four and a half years.

The initial scope of work called for some quality assurance system audits of selected laboratories located in the western United States, laboratory performance audits, a few calibration audits, and technical assistance as requested by the EPA Project Officer.

During the course of the program several modifications to the initial scope of work have occurred. On March 24, 1977, the contract was enlarged to include additional Quality Assurance System Audits and Performance Audits of sites located in Colorado, Utah, and Montana (EPA Region VIII). On August 9, 1977, the contract was further expanded to include Quality Assurance System Audits of seven water quality field stations of the U.S. Geological Survey in Arizona, Colorado, Montana, New Mexico, North Dakota, Utah, and Wyoming.

A major modification to the contract was put into effect on September 13, 1978, when the program was expanded to include approximately sixteen additional organizations, each operating laboratories and air monitoring stations in the Ohio and Tennessee Valleys and in several eastern states in Region III. At the time of the modification the work for Region VIII (initiated on March 24, 1977, as described above) was extended for an additional 12 months. At the request of EPA, the participants of the Ohio and Tennessee Valley groups as well as that of the eastern groups came to and end in April 1979.

On April 27, 1979 another modification was made in the contract requiring the EMSC to conduct additional Quality Assurance System Audits of nine water quality stations of the U.S. Geological Survey in Alabama, Illinois, Indiana, Kentucky, Mississippi, Ohio, Pennsylvania, Tennessee, and Virginia. As part of this effort an executive summary was required covering the seven water sites in 1977 and the nine water sites inspected in 1979.

In this report, reference is made to the Western Quality Assurance Program and to the Eastern Quality Assurance Program. This delineation of the program is employed for convenience in describing work according to the geographical location of the participating groups.

The purpose of the Eastern and Western Quality Assurance Programs was to develop and implement a quality assurance program related to air quality monitoring activities around present and proposed energy development projects. The intent of this program was not to support operators responsible for prevention of significant deterioration (PSD) air monitoring (PSD statutory requirements were not in effect when this program was initiated), but rather to enable the government to utilize and compare air monitoring data from diverse sources for future study and planning purposes by providing information concerning data quality from the monitoring networks. A secondary goal was to provide technical assistance to the participating groups to help them achieve a high level of performance. In the West, the energy projects were located in Montana, South Dakota, North Dakota, Wyoming, Utah, Colorado, Arizona, Nevada, New Mexico, and California. In the East, the energy projects were located in West Virginia, Ohio, Pennsylvania, and Indiana. Additional groups associated with the Eastern QA Program but not involved in energy development projects were located in Delaware, Maryland, Virginia, and the District of Columbia.

The Eastern and Western Quality Assurance Programs were divided into four task areas involving:

1. Quality Assurance System Audits - an initial on-site review of laboratories and field sites;

2. Quality Control Reference Sample Audits - a sample submissions audit program to the laboratories;

3. Calibration Performance Audits - on-site field calibration audits; and

4. Technical assistance to the laboratories, as required.

A separate task involved the preparation and submission of system audit reports of sixteen water quality field stations operated by the U.S. Geological Survey.

All the work carried out by Rockwell in connection with these tasks is summarized in the following sections. Section 2.0 provides an overview with a summary and conclusions; Section 3.0 describes the Quality System Audits; Section 4.0 discusses the results of the Quality Control Reference Sample audits; Section 5.0 summarizes Calibration Performance Audit results; and Section 6.0 describes technical assistance given to the various agencies.

This Final Report is written as a general overview of performance and progress. During the course of the program a very large number of detailed reports was submitted to EPA describing specific tasks. In order to keep this report within manageable size, the reader will oftentimes be directed to these specific reports, should greater detail be required.

SECTION 2

SUMMARY AND CONCLUSIONS

The results described in this report cover the activities of the Western and Eastern Quality Assurance Programs for a period of about four and a half years. During this time Rockwell International personnel with the direction and support of the EPA Project Officer conducted numerous system audits, and provided extensive technical assistance to nearly 30 state, local, and private agencies. The program was characterized by close and continuous interaction between Rockwell and the agencies over a long period of time.

The goals of the program were to enable the government to acquire a large quality assurance data base with which to evaluate air monitoring data from diverse sources, and to provide technical assistance to the participating groups to help them achieve a high level of performance.

It is fair to conclude that both goals have been achieved successfully. The quality assurance data base which is briefly summarized in this final report is indeed very large. Over the four and a half years of the program, Rockwell has sumbitted to EPA over 50 detailed system audit reports, about 75 quarterly laboratory performance audit reports, about 300 individual field calibration performance audit reports, and numerous special reports involving technical assistance activities. These reports have been used by the EPA regional offices as well as the individual participating groups for performance assessment which have led in many cases to substantial improvement in data quality.

The results of the performance audits, both laboratory and field calibration, give clear evidence to steady improvement in overall performance. Regularly scheduled, repeated audits by an external third party provide not only a means for continual self evaluation by the agencies, but also an incentive for the maintenance of high level performance.

SECTION 3

QUALITY ASSURANCE SYSTEM AUDITS

The Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I, [1] defines a system audit as an on-site inspection and review of the quality assurance system used by an agency or group for the total measurement system for each monitoring sensor. A system audit consists of an interview with supervisory and operating personnel and visits to the measurements sites in order to assess and evaluate the following elements of the monitoring program: (a) organization and staffing, (b) personnel training, (c) siting, (d) equipment, (e) operating procedures, (f) quality assurance, (g) preventive maintenance, (h) documentation, and (i) data collection and validation.

AIR MONITORING PROGRAMS

In accordance with the provisions of the Western and Eastern Quality Assurance Programs, a total of 36 laboratories and associated field sites were visited, inspected, and evaluated by EMSC personnel. Tables 1 and 2 list the names of the agencies visited. System audits in the Western QA Program were completed during the first year of the contract, and system audits in the Eastern QA Program were completed during the third year of the contract. Three of the state agencies -- Montana, Utah, and Colorado -- were visited a second time as a result of the expansion in June 1977 in the number of sites audited. A special system audit of Kennecott Minerals Company was conducted in April 1980 at the request of Region VIII.

The mechanics for all system audits were essentially the same. A detailed questionnaire prepared originally by EPA and subsequently modified and enlarged by the EMSC was used as the basis for the interview. In the first system audits the questionnaire was filled out by the auditor on site. In subsequent audits the questionnaire was filled out ahead of time by supervisory personnel of the agency being audited. Much of the discussion was free-flowing and loosely structured, with one question leading to another, as the auditor endeavored to channel the conversation from broad generalizations to precise answers. Interviews generally lasted a day or a day and a half, and the collection of answers formed the basis for the data quality assessment. A detailed report covering the site evaluations was written for each agency, and each agency was given the opportunity to comment upon the preliminary draft of the report. When appropriate, these comments were noted and used in preparing the final report, copies of which were sent to EPA. The final reports contain a great deal of information concerning organization, staffing, laboratory and field equipment, operations and procedures, documentation, data handling, and data validation. The individual reports should be consulted for specific information.

TABLE 1. SUMMARY OF QUALITY ASSURANCE SYSTEM AUDITS PERFORMED IN THE WESTERN QA PROGRAM

Agency	Site Visited	Location	Date *
State of Arizona	Bureau of Air Quality	Phoenix, AZ	12/76
Colorado Oil Shale Tract, C_a	Headquarters	Denver, CO	10/76
	Field Site #1	Rio Blanco, CO	
Colorado Oil Shale tract, C_b	Field Site 023	Rio Blanco, CO	12/76
State of Colorado	Air Quality Surveillance Section	Denver, CO	8/76 and 5/77
	CARIH Station	Denver, CO	
	CAMP Station	Denver, CO	
	Arvada Station	Arvada, CO	
	Welby Station	Welby, CO	
	Greeley Station	Greeley, CO	
	Colorado Springs Station	Colorado Springs, CO	
EPA/Colstrip	Field Site	Colstrip, MT	8/76
EPA/Las Vegas (Lockheed Electronics)	Laboratory	Las Vegas, NE	10/76
State of Montana	Air Quality Bureau	Helena, MT	8/76 and 5/77
	Colstrip Trailer	Colstrip, MT	
	Lame Deer	Lame Deer, MT	
	C Hill	Anaconda, MT	
	Highway Junction	Anaconda, MT	
	Saddle Mountain	E. Helena, MT	
	Microwave	E. Helena, MT	
	Alpine West	Butte, MT	
Montana Power Company	Field Site #3	Colstrip, MT	8/76
State of New Mexico	Air Quality Bureau	Santa Fe, NM	9/76

(Continued)

TABLE 1. (Continued)

Agency	Site Visited	Location	Date *
State of New Mexico (Continued)	Albuquerque Field Sites Four Corners Area Sites	Albuquerque, NM Farmington, NM	9/76
National Oceanic and Atmospheric Administration (NOAA)	Headquarters	Boulder, CO	12/76
State of North Dakota	State Dept. of Health Stanton Beulah	Bismarck, ND Stanton, ND Beulah, ND	8/76
Northern Testing Laboratory	Laboratory	Billings, MT	8/76
State of South Dakota	State Laboratory	Pierre, SD	8/76
Utah Oil Shale Tracks, U_a/U_b	Field Site A-6	Bonanza, UT	9/76
State of Utah	Bureau of Air Quality Price Huntington Salt Lake City Magna Bountiful Ogden Provo	Salt Lake City, UT Price, UT Huntington, UT Salt Lake City, UT Magna, UT Bountiful, UT Ogden, UT Provo, UT	9/76 and 5/77
Ute Research Laboratory	Laboratory	Fort Duchesne, UT	9/76

(Continued)

TABLE 1. (Continued)

Agency	Site Visited	Location	Date *
State of Wyoming	Laboratory Headquarters	Cheyenne, WY	2/76
	Newcastle Field Site	Newcastle, WY	
	Gillette Field Site	Gillette, WY	
	Patrick Draw Field Site	Rock Springs, WY	
Yellowstone County	Laboratory	Billings, MT	8/76
	Billings Field Site	Billings, MT	
	Laurel Field Site	Laurel, MT	
Kennecott Minerals	Headquarters	Salt Lake City, UT	4/80
	Magna Field Site	Magna, UT	
	Calibration and Repairs Shop	Magna, UT	

* Date of the on-site visit by Rockwell personnel.

TABLE 2. SUMMARY OF QUALITY SYSTEM AUDITS PERFORMED IN THE EASTERN QA PROGRAM*

Agency	Date		Date
City of Alexandria	8/78	Ohio Edison	2/79
Allegheny County	9/78	Pennsylvania Electric Co.	3/79
City of Baltimore	10/78	State of Pennsylvania	9/78
Baltimore County	10/78	City of Philadelphia	10/78
City of Cincinnati	2/79	RAPCA - Dayton, Ohio	2/79
State of Delaware	10/78	State of Virginia	8/78
Fairfax County	8/78	Washington, DC	8/78
State of Indiana	2/79	State of West Virginia	9/78
State of Maryland	10/78		

* Date of the on-site visit by Rockwell personnel.

The findings were summarized in each report as a table of recommendations given to the individual agency. The table lists deficiencies found, recommended solutions, approximate cost to implement the solutions, and an estimate of the impact of each deficiency on the quality of the data. Table 3 shows a typical list of recommendations. While most of the agencies over the course of the time have implemented many of the recommendations, consistent with their budgetary constraints, the follow-up of the recommendations is beyond the scope of this contract.

The intent of this final report is not to list the deficiencies found for each agency; the original reports should be examined for this purpose. However many of the deficiencies were found to be prevalent throughout all the agencies, and it is appropriate to generalize our findings.

The one major deficiency found in the operation of most of the agencies audited was the lack of a comprehensive written quality assurance plan. While many agencies designated some individual to be the parttime quality assurance coordinator, the duties and authority of this individual were almost never well defined or effectively implemented. Because QA Plans were not thoroughly developed, deficiencies associated with poor documentation, lack of written operating procedures, inadequate quality controls, and non-traceable standards were widespread among most of the agencies.

Since the beginning of the program in 1976 EPA and the state agencies have recognized this problem and have attempted to correct it. The major

TABLE 3. TYPICAL SYSTEM AUDIT SUMMARY LIST OF RECOMMENDATIONS

Deficiency	Recommendation	Approximate Cost	Impact on Data
No written QA plan.	Prepare, review, and implement QA procedures.	Approximately 2 man months.	Difficult to defend current data in an adversary situation.
No written O&M Manual.	Prepare, review, and implement uniform operating procedures.	Approximately 2 man-months.	Difficult to defend current data in an adversary situation.
No QA officer.	Appoint a QA officer to implement QA procedures.	Initially position should be full time. After QA procedures are implemented, position could drop to 1/2 to 3/4 time.	Difficult to defend current data in an adversary situation.
Some SO_2 analyzers are not "equivalent".	Replacement is necessary if data is to be used for PSD monitoring.	About $6,000. per analyzer.	PSD data not acceptable unless instruments are "equivalent".
Calibration procedure for SO_2 not uniform.	Adopt uniform procedure. Include in QA plan and O&M Manual.	Included above.	Difficult to defend current data in an adversary situation.
SO_2 inlet system and particulate filter made of metal.	Replace with glass or Teflon.	Several hundred dollars per station.	May affect incoming SO_2 concentration.
Zero and span data not recorded.	Record data. Use it for assessment of drift.	Negligible.	Difficult to defend current data in an adversary situation.
No check of temperature of permeation tube holder.	Verify temperature with NBS traceable thermometer.	Precision thermometer available for under $100.	Difficult to defend current data in an adversary situation.
Uncertain calibration frequency.	Adopt a calibration schedule and enforce implementation.	Probably negligible. May require changing priorities.	Difficult to defend current data in an adversary situation.

(Continued)

TABLE 3. (Continued)

Deficiency	Recommendation	Approximate Cost	Impact on Data
Uncertain definitions of performance control.	Adopt uniform rules. Define valid data. Include in O&M Manual and QA plan.	Included in cost of preparing QA plan.	Difficult to defend current data in an adversary situation.
Hi-vol filters are not inspected for pinholes.	Examine filters using a light box prior to weighing.	Negligible.	May affect data quality.
Analytical balance not checked frequently enough.	Check balance with Class S weights every time filters are weighed.	Class S weights available for several hundred dollars.	Difficult to defend current data in an adversary situation.
No internal or external audits are being performed.	Initiate procedures for internal and external audits. Describe in QA plan.	Depends on magnitude of program. If QA officer performs audits, his job would become a full time position. Audit equipment could cost 10-20K.	Difficult to defend current data in an adversary situation.

mechanism for carrying out this intent is the adoption and promulgation of the Ambient Air Quality Surveillance provisions issued by EPA in 40 CFR Part 58 on May, 10, 1979.[2] This part of the Code of Federal Regulations contains criteria and requirements for ambient air quality monitoring, including:

1. Quality Assurance procedures
2. Monitoring methodology
3. Operating schedules
4. Siting parameters.

As state and local agencies, as well as private operators begin to implement the requirement of 40 CFR Part 58, many of the deficiencies uncovered in the system audits will undoubtedly disappear.

U.S. GEOLOGICAL SURVEY FIELD STATIONS

The Environmental Monitoring & Services Center (EMSC) of Rockwell International, under contract with the Environmental Protection Agency (EPA), conducted an evaluation survey of several field laboratories of the United States Geological Survey (USGS). The purpose of this survey was an evaluation of the quality assurance (QA) practices employed by these laboratories in the area of water quality and a comparison with the practices of EPA. A total of sixteen laboratories were evaluated. Seven were located in the energy development area of the Western states and the rest were in the Eastern and Midwestern energy belt. Table 4 gives the laboratories which were surveyed and the date of the evaluation visit. As indicated in the table, the total effort was completed in two distinct time periods which were twenty-one months apart. The Western survey was conducted in September 1977 and the Midwestern and Eastern surveys were conducted in July/August 1979.

The procedures used for the evaluation of each laboratory were similar. First, each laboratory was requested to respond to the EPA questionnaire. The completed questionnaire forms were then returned to EMSC, where they were evaluated for completeness and clarity, and examined for identification of items which required further discussion. After this, the person in charge of each laboratory was contacted by telephone and the date for the inspection visit set. Each laboratory inspection opened with a brief presentation of the program to the USGS personnel and a discussion of the questionnaire. This was followed by a physical inspection of all the laboratory operations related to water quality, including mobile units and sampling sites, and the visit was concluded with an exit debriefing.

The activities of each individual laboratory were reported in separate formal reports. In these reports the findings of the overall survey which include general laboratory facilities, laboratory functions, quality assurance and data handling are discussed and compared collectively and general conclusions are shown.

TABLE 4. SUMMARY OF THE USGS LABORATORIES SURVEYED

USGS Laboratory Operations		Date of Survey
Western Energy Program	Salt Lake City, UT	September 14, 1977
	Vernal, UT	September 15, 1977
	Yuma, AZ	September 16, 1977
	Albuquerque, NM	September 26, 1977
	Cheyenne, WY	September 27, 1977
	Bismarck, ND	September 28, 29, 1977
	Helena, MT	September 30, 1977
Midwest and Eastern Energy Group	Louisville, KY	July 25, 1979
	Nashville, TN	July 26, 1979
	Tuscaloosa, AL	July 27, 1979
	Jackson, MS	July 30, 1979
	Richmond, VA	July 31, 1979
	Harrisburg, PA	August 1, 1979
	Columbus, OH	August 2, 1979
	Champaign, IL	August 2, 1979
	Indianapolis, IN	August 3, 1979

The findings of the overall survey were summarized in an executive summary report covering all sixteen laboratories. This report was written by Dr. George Colovos and Dr. Matt Yoong and submitted to the Project Officer in June 1978. The summary report as well as the individual laboratory reports should be consulted for specific details. The reports may be obtained by contacting the Environmental Monitoring and Suport Laboratory in Cincinnati, Ohio.

SECTION 4

QUALITY CONTROL REFERENCE SAMPLE AUDITS

INTRODUCTION

Regularly scheduled Quality Control Reference Sample Audits have been carried out for the following analyses or measurements: (1) sulfate/nitrate ($SO_4^=/NO_3^-$) analysis; (2) sulfur dioxide (SO_2) analysis; (3) nitrogen dioxide (NO_2) analysis; (4) carbon monoxide (CO) analysis; (5) weighing performance; and (6) high volume flow rate measurement.

The tables appearing in this section list all the surveys performed during the four years of the program by date. Participating laboratories in each survey are indicated by a check (✓) mark.

In the chemical analysis survey for $SO_4^=/NO_3^-$, SO_2, and CO, Rockwell obtained from commercial vendors, either directly or through EPA, multiple sets of the appropriate samples. Five or ten replicate samples were first analyzed at Rockwell, and the mean value of the analyses was by definition the "true" value. Samples were then submitted for analysis to the participating laboratories. Laboratories generally analyzed only one sample of each concentration, although ocassional duplicate samples were included in the set without the knowledge of the laboratory. The results of all the participants were compared to the "true" value to determine their accuracy.

To assure the correctness of the Rockwell "true" value, several internal and external quality control procedures were used. Internal quality control procedures in the Rockwell laboratory included comparison of analyses of replicate samples, comparison of every new stock standard solution with the old solution, duplicate calibraton curves before and after analysis, analysis of quality control standards every 10 samples, and maintenance of routine quality control limits. External quality control was provided by comparing the Rockwell "true" value with the mean value obtained through replicate sample analysis by either the Quality Assurance Division (QAD-EMSL) laboratory or by the vendor. This comparison was included in each report.

Laboratory performance was evaluated by several methods. The most direct method was to compare the concentration determined by each laboratory with the "true" value as determined by Rockwell. Linear graphs were prepared in which the laboratory values were plotted against the "true" values. The slope, intercept, and correlation coefficient for each laboratory line were then tabulated as indices of performance. Perfect agreement between a laboratory's results and Rockwell's "true" value for all analyses results in a straight

line with unit slope, zero intercept, and a correlation coefficient equal to 1.0000.

The slope of the line is a good measure of overall analytical accuracy, provided that the intercept is small compared to the concentrations being analyzed. If the slope is near 1.0, a large intercept indicates a bias in the analysis which might be caused by such errors as incorrect blank corrections or contaminants in the water supply.

A second method for evaluating laboratory performance was to calculate average percent differences between the laboratory analysis values and the "true" values. The average percent differences were tabulated for each laboratory that participated in the quarterly audit as measures of analytical error. The calculations are explained in detail in 40 CFR Part 58 Ambient Quality Surveillance - Appendix A: Quality Assurance Requirements for State and Local Air Monitoring Stations (SLAMS). (3) The major difference between the Rockwell procedure and that described in the SLAMS regulations is that the latter specifies three concentration ranges: 0.2 - 0.3 μg/ml; 0.5 - 0.6 μ g/ml; and 0.8 - 0.9 μg/ml for both SO_2 and NO2. In the current Rockwell program there are three to six samples and the concentration of the audit samples cover a much wider range. Another difference from the EPA regulations is that our program included audits of CO, $SO_4^=$, and NO_3^- analysis, none of which is required by the new regulation.

The composite performance of all laboratories participating in the surveys is summarized in tables 5 through 17. for each of the pollutants independently. Data are presented in tables showing for each calendar quarter the average percent difference $\bar{D}$, standard deviation (S_a), and the slope and intercept of the linear graphs. Detailed results for the performance of each individual laboratory are tabulated for each pollutant in quarterly reports which were submitted to EPA.

Composite averages were obtained by combining the quarterly results of each agency using the following equations:

$$\bar{D} = \frac{\sum_{j=1}^{k} n_j \bar{d}_j}{\sum_{j=1}^{k} n_j} \qquad (1)$$

$$S_a = \sqrt{\frac{\sum_{j=1}^{k} (n_j - 1)\, S_j^2}{\sum_{j=1}^{k} (n_j - 1)}}\,, \qquad (2)$$

where $\bar{D}$ and S_a are the composite average percent deviation and the standard deviation, respectively, n_j is the number of samples analyzed by the j^{th} laboratory, $\bar{d}_j$ is the average percent difference for all samples analyzed by the j^{th} laboratory, S_j is the standard deviation, and k is the total number of participating laboratories. In order to avoid undue bias of the results, a laboratory was declared an outlier and the data were not used for computing composite averages if the average percent deviation $\bar{d}_j$ or the standard deviation S_j for that laboratory was equal to or greater than 100 percent. The latter value was chosen arbitrarily so as to eliminate only grossly erroneous data (e.g., decimal point error in the reported data).

To evaluate progress or improvement in overall performance, tables have been prepared showing the percentage of all the analyses in which the error was equal or less than certain specified values, usually 10 or 20%. These values were selected as reasonable targets for analytical accuracy which a large fraction of the laboratories could be expected to meet or exceed. The tables list results for selected sample concentration ranges for each year of the program. The concentration ranges were chosen so that the number of analyses in each range was roughly equal. The results for each year were obtained by combining the results from the quarterly reports as follows:

Year:	4th quarter 1976
	1st quarter 1977
	2nd quarter 1977
	3rd quarter 1977
Year:	4th quarter 1977
	1st quarter 1978
	2nd quarter 1978
	3rd quarter 1978, etc.

SULFATE/NITRATE ANALYSIS

All of the sulfate/nitrate performance surveys performed since the inception of this program are summarized in Table 5. This performance survey required participating laboratories to analyze a set of four to six filter strips spiked with varying amounts of sulfate and nitrate ions. At least 10 sets of filters presumed to be identical to those analyzed by the laboratories were analyzed by the Rockwell Chemistry Laboratory using the methylthymol blue procedure for $SO_4^=$ and the copperized cadmium reduction method for NO_3^-. In the interpretation of results, no bias or adjustment was made for the fact that laboratories included in the surveys used methods different from Rockwell's. All laboratories used EPA accepted methods which presumably give equivalent results, making such adjustments unnecessary.

Table 6 lists the various composite comparison parameters for $SO_4^=$ audits, and Table 7 lists the same comparison parameters for NO_3^- audits. From the results shown in these tables it is difficult to state unequivocally whether there was any improvement or not in overall performance.

BEGIN FIRST LINE OF TEXT HERE
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD SECTIONS HERE
BEGIN LAST LINE OF TEXT
3/8"
PAGE NUMBER
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
EPA Form 2350-4 (4-80)
(PREVIOUSLY CIR. EPA FORM 287)
TYPING GUIDE SHEET

TABLE 5. LIST OF PARTICIPANTS IN THE INTERLABORATORY PERFORMANCE SURVEY FOR $SO_4^=/NO_3^-$

Agency	Survey Date by Quarter															
	4/76	1/77	2/77	3/77	4/77	1/78	2/78	3/78	4/78	1/79	2/79	3/79	4/79	1/80	2/80	3/80
Western																
Arizona State	✓†	✓†	✓†	✓†	✓†	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Colorado State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Energy & Environmental Resource Consultants, Inc.							✓	✓	✓	✓	✓	✓				
Montana State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
New Mexico State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
North Dakota State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Northern Testing Lab	✓	✓	✓	✓	✓	✓										
South Dakota State						✓	✓	✓								
Ute Research			✓	✓	✓	✓	✓	✓	✓	✓						
Eastern																
Indiana State									✓	✓						
Maryland State									✓	✓						
Pennsylvania State									✓	✓						
Philadelphia City									✓	✓						
Virginia State									✓	✓						
West Virginia State									✓	✓						
EPA, RTP	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

* A check denotes that the agency participated in the survey

† SO_4 only

TABLE 6. COMPOSITE PERFORMANCE FOR $SO_4^=$ AUDITS

Quarter	Ave % Diff $\bar{d}_j$	Std Dev (%) S_j	Slope	Intercept ($\mu g/m^3$)
4/76	0.7	29.3	0.971	0.164
1/77	5.9	7.8	1.075	-0.127
2/77	-5.3	12.8	0.948	0.106
3/77	-4.0	21.5	0.946	0.163
4/77	-0.6	13.0	1.010	-0.151
1/78	-5.5	24.6	1.095	-0.385
2/78	10.8	31.8	0.993	0.505
3/78	4.9	19.6	1.051	0.131
4/78	-2.8	18.1	0.984	-0.178
1/79	2.5	22.3	0.958	0.429
2/79	0.4	9.3	1.072	-0.529
3/79	2.8	10.6	0.963	0.554
4/79	-2.9	4.2	0.937	0.421
1/80	-0.8	9.8	0.948	0.288
2/80	0.1	4.8	1.003	-0.085
3/80	1.2	23.2	0.935	0.976

Tables 8 and 9 are perhaps more illuminating. These tables show that the percentage of all the $SO_4^=$ analyses in which the error was equal or less than 10% increased from 55% on year 1 to 82% on year 4. The corresponding percentages for NO_3^- analyses was 43% on year 1 to 72% on year 4. The improvement in performance over the four year period is thus clearly evident. In the fourth year of the program 70-80% of all analyses had errors of less than 10%.

Tables 8 and 9 do not show striking differences in analytical performance between sample concentrations, although as expected the smallest samples result in the lowest fraction of analyses with error of 10% or less. Sample ranges in these tables are given in units of $\mu g/m^3$ since the air flow for these audits was assumed to be 2000 m^3, and the strips were assumed to repre-

TABLE 7. COMPOSITE PERFORMANCE FOR NO_3^- AUDITS

Quarter	Ave % Diff $\bar{d}_j$	Std Dev (%) S_j	Slope	Intercept ($\mu g/m^3$)
4/76	24.6	46.7	1.058	0.120
1/77	4.3	13.8	0.977	0.338
2/77	0.0	10.3	0.993	0.035
3/77	4.8	8.7	1.015	0.075
4/77	1.3	12.1	0.918	0.154
1/78	5.6	14.8	1.048	0.012
2/78	-1.2	31.0	1.080	-0.234
3/78	13.0	7.1	1.109	0.039
4/78	2.1	24.6	1.002	0.146
1/79	1.0	7.6	1.011	-0.065
2/79	-7.8	12.1	0.862	0.153
3/79	-0.3	8.1	1.061	0.310
4/79	-5.7	5.5	0.918	0.130
1/80	16.2	24.6	1.083	0.220
2/80	-8.8	8.6	0.933	-0.137
3/80	2.2	4.1	1.066	-0.354

sent 1/12 of a standard high-volume filter; the weight in μg of sample actually analyzed can be obtained from the sample concentration simply by multiplying by the ratio 2000/12.

SULFUR DIOXIDE

Sulfur dioxide samples consisted of standard ampules containing freez-dried solutions of sodium sulfite and tetrachloromercurate. The "true" value for each sample was obtained by the Rockwell laboratory by analysis of at least 10 replicate samples. Table 10 lists the participants in the SO_2 surveys during the course of the program. Table 11 summarizes the composite results. As with SO_4^-/NO_3^-, the results in this table are difficult to interpret and are shown for the sake of completeness.

TABLE 8. SUMMARY OF AGENCY PERFORMANCE FOR $SO_4^=$ ANALYSIS

Sample Concentration Range* $\mu g/m^3$	Percent Analyses With Error ≤ 10%				Percent Analyses With Error ≤ 20%			
	Yr 1	Yr 2	Yr 3	Yr 4	Yr 1	Yr 2	Yr 3	Yr 4
1-5	47	38	36	61	59	62	67	89
5-15	58	77	66	88	80	91	87	100
15-25	63	80	77	79	88	88	92	98
> 25	50	48	79	90	88	78	93	100
All	55	62	67	82	75	80	86	98

* The air flow was assumed to be 2000 m^3, and the filter strips were assumed to represent 1/12 of a standard high-volume filter. Thus the weight in μg of the sample actually analyzed is obtained by multiplying the sample concentration in $\mu g/m^3$ by the ratio 2000/12.

TABLE 9. SUMMARY OF AGENCY PERFORMANCE FOR ANALYSIS OF NO_3^-

Sample Concentration Range* $\mu g/m^3$	Percent Analyses With Error ≤ 10%				Percent Analyses With Error ≤ 20%			
	Yr 1	Yr 2	Yr 3	Yr 4	Yr 1	Yr 2	Yr 3	Yr 4
0-2	29	38	40	67	47	71	79	83
2-5	56	27	59	83	81	87	82	89
5-9	44	56	72	69	73	89	87	82
9-14	53	71	70	75	88	95	88	83
All	43	51	63	72	69	83	85	83

* The air flow was assumed to be 2000 m^3, and the filter strips were assumed to represent 1/12 of a standard high-volume filter. Thus the weight in μg of the sample actually analyzed is obtained by multiplying the sample concentration in $\mu g/m^3$ by the ratio 2000/12.

TABLE 10. LIST OF PARTICIPANTS IN THE INTERLABORATORY PERFORMANCE SURVEY FOR SO_2

Agency	Survey Date by Quarter													
	4/76	2/77	3/77	4/77	1/78	2/78	3/78	4/78	2/79	3/79	4/79	1/80	2/80	3/80
Arizona State	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Colorado State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓			✓	
Energy & Environmental Resource Consultants, Inc.														
Lockheed		✓				✓	✓	✓	✓	✓				
Montana State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓		
New Mexico State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
North Dakota State	✓	✓	✓	✓	✓	✓	✓	✓						
Northern Testing Lab	✓	✓	✓	✓	✓									
Northrop Services Inc.				✓		✓	✓							
South Dakota State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
Wyoming State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Yellowstone County	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
Cincinnati City								✓	✓					
Dayton City								✓	✓					
West Virginia State								✓	✓					
Indiana State								✓	✓					
Maryland State								✓						
Pennsylvania State								✓	✓					
Philadelphia City								✓	✓					
Fairfax County								✓	✓					
EPA,RTP	✓	✓	✓	✓			✓	✓	✓	✓	✓	✓	✓	✓

Table 12 shows the percentage of analyses with error equal or less than 10% and 20%. The table indicates that in the first three years of the program the fraction of all the analyses with error of 10% or less remained nearly constant at about 65%, while in the last year the fraction of analyses with error of 10% or less increased to 83%. In all four years the fraction of analyses with error of 10% or less was significantly lower for samples below 20 $\mu g/m^3$ than for the higher concentration samples. (Note: the sample concentration is given in $\mu g/m^3$. For the SO_2 audits the air volume was assumed to be 300 liters, and the sulfite salt was dissolved in 50 ml of solution. Thus to convert $\mu g/m^3$ to $\mu g/ml$ multiply the sample range given in Table 12 by the ratio 0.300/50.)

NITORGEN DIOXIDE ANALYSIS

Nitrogen dioxide samples consisted of standard ampules containing solutions of sodium nitrite. The "true" value for each sample was obtained in the

TABLE 11. COMPOSITE PERFORMANCE FOR SO_2 AUDITS

Quarter	Ave % Diff $\bar{d}_j$	Std Dev (%) S_j	Slope	Intercept ($\mu g/m^3$)
4/76	-2.0	18.0	1.038	-3.474
1/77	-7.8	14.1	0.962	-2.264
3/77	-9.4	11.4	0.952	-1.973
4/77	-15.4	25.9	0.883	-1.028
1/78	1.0	13.8	0.989	0.975
2/78	-4.6	15.5	0.943	2.256
3/78	2.6	12.0	1.048	-1.598
4/78	-5.2	19.4	1.018	-2.256
2/79	2.3	24.9	1.003	-0.335
3/79	-5.7	10.5	1.008	-2.492
4/79	-2.2	7.1	0.994	-0.575
1/80	1.5	14.0	0.997	0.828
2/80	-4.8	12.8	1.014	-2.531
3/80	2.6	3.0	1.010	0.939

TABLE 12. SUMMARY OF AGENCY PERFORMANCE FOR SO_2 ANALYSIS

Sample Concentration Range * $\mu g/m^3$	Percent Analyses With Error ≤ 10%				Percent Analyses With Error ≤ 20%			
	Yr 1	Yr 2	Yr 3	Yr 4	Yr 1	Yr 2	Yr 3	Yr 4
10-20	39	38	21	28	54	64	36	67
35-85	58	68	65	89	88	81	76	98
90-130	83	78	89	100	93	84	89	100
150-230	79	73	77	96	93	83	85	100
All	63	66	65	83	83	79	73	94

* The air flow was assumed to be 300 liters, and the sulfite salt was dissolved in 50 ml of solution. To convert sample concentration from $\mu g/m^3$ to $\mu g/ml$ multiply by the ratio 0.300/50.

TABLE 13. LIST OF PARTICIPANTS IN THE INTERLABORATORY PERFORMANCE SURVEY FOR NO_2

Agency	Survey Date by Quarter																			
	1/77	2/77	3/77	4/77	1/78	2/78	3/78	4/78	1/79	2/79	3/79	4/79	1/80	2/80						
Arizona State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓						
Colorado State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓						
Energy & Environmental Resource Consultants, Inc.																				
Montana State	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓									
New Mexico State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓							
North Dakota State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓						
Northern Testing Lab	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓									
South Dakota State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓						
Wyoming State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓						
Indiana State								✓	✓	✓	✓	✓	✓	✓						
Pennsylvania State								✓	✓	✓										
Philadelphia City #1								✓	✓											
Maryland State								✓	✓	✓										
Virginia State								✓	✓	✓										
Fairfax County								✓	✓	✓										
Cincinnati City								✓	✓	✓										
Philadelphia City #2								✓	✓	✓										
Dayton, Ohio										✓										
EPA, RTP	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓						

Rockwell laboratory by analysis of at least 10 replicate samples. Table 13 lists the agencies participating in this performance survey since the beginning of the program.

Table 14 summarizes the composite results. A close examination of this table and comparison with the corresponding results for $SO_4^=$, NO_3^-, and SO_2 indicate clearly that the analytical results for NO_2 are significantly better than for the other three analytes. This is shown by the fact that the composite average percent difference and standard deviation of the percent differences are relatively low, particularly in the last three years of the program. Table 15 confirms this assessment, since except for the first year over 80% of all the analyses showed errors of 10% or less. In the fourth year of the program over 90% of the analyses resulted in errors of 10% or less. In general the higher the sample concentration, the better the results.

TABLE 14. COMPOSITE PERFORMANCE FOR NO_2 AUDITS

Quarter	Ave % Diff $\bar{d}_j$	Std Dev (%) S_j	Slope	Intercept ($\mu g/m^3$)
1/77	9.4	20.3	1.013	0.017
2/77	-8.9	15.0	0.935	-0.010
3/77	-1.0	14.3	0.961	0.006
4/77	-3.7	14.9	0.982	-0.004
1/78	5.3	6.3	0.999	0.016
2/78	3.2	6.2	0.968	0.015
3/78	-6.8	3.7	0.973	-0.018
4/78	0.3	12.1	1.030	-0.012
1/79	-0.6	4.9	0.981	0.005
2/79	-0.1	6.9	0.969	0.013
3/79	2.6	5.1	1.004	0.007
4/79	-1.8	4.9	0.984	-0.002
1/80	-4.1	2.4	0.975	-0.008
2/80	-2.9	2.8	0.974	-0.002

TABLE 15. SUMMARY OF AGENCY PERFORMANCE FOR ANALYSIS OF NO_2

Sample Concentration Range * $\mu g/m^3$	Percent Analyses With Error ≤ 10%				Percent Analyses With Error ≤ 20%			
	Yr 1	Yr 2	Yr 3	Yr 4	Yr 1	Yr 2	Yr 3	Yr 4
0.10-0.21	31	43	56	92	64	77	100	100
0.22-0.38	72	84	74	95	97	98	88	100
0.39-0.68	75	95	90	85	94	98	96	100
0.69-1.02	81	100	92	93	93	100	95	98
All	64	83	86	91	87	94	94	99

TABLE 16. LIST OF PARTICIPANTS IN THE INTERLABORATORY PERFORMANCE SURVEY FOR CO

Agency	Survey Date by Quarter												
	4/76	1/77	3/77	4/77	1/78	2/78	3/78	1/79	3/79	4/79	1/80	2/80	3/80
Albuquerque	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Arizona State	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	
Colorado State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Montana State		✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓
New Mexico State	✓	✓	✓	✓	✓	✓			✓	✓	✓	✓	✓
Utah State	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Yellowstone County	✓												
EPA, RTP	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Alexandria City								✓					
Delaware State								✓					
Dayton City								✓					
Alleghany County								✓					
Maryland State								✓					
Philadelphia City								✓					
Washington DC								✓					
Pennsylvania State								✓					
Fairfax County								✓					
Cincinnati City								✓					
Virginia State								✓					
West Virginia State								✓					
Indiana State								✓					

CARBON MONOXIDE ANALYSIS

Table 16 lists all the participants in the CO survey by quarter of performance. Carbon monoxide samples were contained in 0.85 m^3 (30 ft^3) aluminum cylinders. Three different concentrations were submitted for analysis in each survey. Replicate analyses were performed in the Rockwell Quality Assurance Laboratory using a Bendix non-dispersive infrared analyzer, and an NBS Standard Reference Material (SRM) cylinder containing 95.0 ppm CO in air used as the standard. The "true" value was established by analysis of at least five cylinders of each concentration.

The results of all CO surveys were for the most part very satisfactory. Table 17 presents composite data for all the quarters. Table 18 summarizes the agency performance by showing the fraction of all the analyses in which the error was equal or less than 5% and 10%. The lower target error of 5% was used because of the relatively good results for CO. Table 18 shows that the fraction of all the analyses with error of 5% or less increased from 60% in

TABLE 17. COMPOSITE PERFORMANCE FOR CO AUDITS

Quarter	Ave % Diff $\bar{d}_j$	Std Dev (%) S_j	Slope	Intercept ($\mu g/m^3$)
4/76	1.4	6.7	1.011	0.065
1/77	1.1	4.4	1.009	-0.004
2/77	1.1	10.1	1.037	-0.395
4/77	-0.7	9.5	0.996	-0.009
1/78	-2.8	5.0	0.987	-0.248
2/78	-2.1	7.3	0.999	-0.301
3/78	-0.7	5.2	1.014	-0.308
1/79	-3.1	3.7	0.987	-0.270
3/79	0.1	6.6	1.019	-0.252
4/79	0.8	13.2	1.015	-0.142
1/80	0.2	3.1	0.992	0.035
2/80	-0.9	4.0	1.002	-0.170
3/80	-2.5	5.2	1.012	-0.438

TABLE 18. SUMMARY OF AGENCY PERFORMANCE FOR ANALYSIS OF CO

Sample Concentration Range ppm	Percent Analyses With Error ⩽ 5%				Percent Analyses With Error ⩽ 10%			
	Yr 1	Yr 2	Yr 3	Yr 4	Yr 1	Yr 2	Yr 3	Yr 4
3-10	34	45	54	63	76	67	82	79
15-30	73	77	82	92	97	97	97	97
34-50	73	91	89	93	96	100	95	100
All	60	71	75	82	90	88	91	92

TABLE 19. LIST OF PARTICIPANTS IN THE PERFORMANCE AUDITS FOR WEIGHING AND HI-VOL FLOW CALIBRATION

	Survey and Date of Report						
	WEIGHING			HI-Vol			
	8/77	3/78	7/79	8/77	4/78	9/79	8/80
Western							
Albuquerque	✓	✓	✓	✓	✓	✓	✓
Arizona State	✓	✓	✓	✓	✓	✓	✓
Colorado Oil Shale Tract, C-a	✓	✓	✓	✓	✓	✓	✓
Colorado Oil Shale Tract, C-b	✓	✓	✓	✓	✓	✓	✓
Colorado State	✓	✓	✓	✓	✓	✓	✓
Energy & Environmental Resources Consultants, Inc.			✓		✓	✓	✓
Montana State	✓	✓	✓	✓	✓	✓	✓
Montana Power Co.				✓	✓	✓	✓
New Mexico State	✓	✓	✓	✓	✓	✓	✓
North Dakota State	✓	✓	✓	✓	✓	✓	✓
Northern Testing Lab	✓	✓					
South Dakota State	✓	✓	✓	✓	✓	✓	✓
Utah Oil Shale Tract, Ua/Ub	✓	✓	✓	✓	✓	✓	✓
Ute Research	✓	✓	✓	✓	✓		
Utah State	✓	✓	✓	✓	✓	✓	✓
Wyoming State	✓	✓	✓	✓	✓	✓	✓
Yellowstone County	✓	✓	✓	✓	✓	✓	✓
Eastern							
Maryland			✓			✓	✓
Delaware			✓			✓	✓
Philadelphia City			✓			✓	✓
Cincinnati, Ohio			✓			✓	✓
Indiana State			✓			✓	✓
Pennsylvania State			✓			✓	✓
Allegheny County			✓			✓	✓
West Virginia State			✓			✓	✓
Virginia State			✓			✓	✓
Alexandria, Virginia			✓			✓	✓
Fairfax County			✓			✓	✓
Washington, DC			✓			✓	✓
Dayton, Ohio			✓			✓	✓

the first year to 82% in the fourth year. In all four years of the program approximately 90% of all the analysis resulted in errors of 10% or less. The close agreement between the various agencies and Rockwell is probably due to the fact that agencies use cylinders for calibration that contain CO at ambient levels and require no dilution. The CO concentratrations supplied by vendors are in most cases apparently reliable for this particular analysis.

WEIGHING SURVEY

Three weighing performance audits were conducted to test weighing accuracy of the participating laboratories. The audits were conducted in 1977, 1978, and 1979. Table 19 lists the participants in both the weighing and the high-volume flow calibration audits which are discussed below. For weighing audits twelve sets of 3 weights, each containing a 1, 2, and 5g weight, slightly modified by filing away some of the mass, were cleaned and weighed several times on two different balances over a period of several days. Each balance was calibrated just prior to use with an NBS certified set of Class S weights. One set was sent to each participating agency, which then weighed the objects and reported results to Rockwell. The objects were reweighed after return to insure that no significant change had occurred during transit.

Table 20 summarizes the weighing results for each of the three surveys. In general weighing performance has been quite satisfactory. In 1977 three agencies out of sixteen reported weights which differed from the "true" weights by more than 1 mg. In 1979 three agencies out of twenty-eight had a weighing problem. In most cases the weight differences were traceable to faulty balances.

HIGH-VOLUME FLOW RATE CALIBRATION AUDITS

A flow rate calibration audit was conducted during each year of the program. A list of participants by date is given in Table 18. The audit kits, known as ReF (reference flow) devices, were calibrated in the Rockwell QA laboratory using a Roots meter according to the procedure described in Appendix B, "National Primary and Secondary Ambient Air Standards."[4]

For the field tests the participants were asked to install the ReF device on the field sampler and to measure the flow with each of the five resistance plates inserted in the device to restrict the flow. From the reported pressure drop ΔP across the fixed orifices of the ReF device, as well as the measured ambient barometric pressure and temperature, Rockwell calculated the "true" flow and compared it to the value reported by the agency. In making these comparisons the appropriate temperature and pressure corrections were made to allow for the fact that ambient field conditions are normally different from those in the laboratory where the ReF device is calibrated.

To evaluate the results obtained at each site the flows measured by the agency were plotted against the "true" flows calculated by Rockwell and linear constants were derived from the graph. A calibration error was then calculated as the percent difference between the flow measured by the agency and the "true" flow when the latter is taken as 1.132 cubic meters per minute (CMM).

TABLE 20. SUMMARY OF AGENCY PERFORMANCE FOR WEIGHING AUDIT

	Year 1 1977			Year 2 1978			Year 3 1979		
No. of Agencies Participating	16			15			28		
Nominal Weight	1g	2g	5g	1g	2g	5g	1g	2g	5g
Total Number of Weighings	19	19	19	17	17	17	30	30	30
No. of Weighings With Difference of 0.5 mg or less	14	12	14	14	15	14	21	21	20
No. of Weighings With Difference of 1.0 mg or less	15	14	15	17	17	17	28	27	28

The value of 1.132 CMM (40 cubic feet per minute) was chosen arbitrarily since it is the nominal flow commonly used by many agencies.

A few agencies used flow controllers which did not allow for flow changes. For these cases the calibration error was simply the percent difference between the flow measured by the agency and the flow calculated by Rockwell.

Table 21 presents a summary of the results of the four performance audits. The table gives the percent of sites in which the calibration error falls within the specified error ranges shown in the first column. The data of Table 21 is also shown graphically in Figure 1. The histograms in Figure 1 illustrate how the performance has improved in the four years of the program. In the first year only 20% of the surveyed sites reported errors of less than 5%, whereas in the third and fourth years the fraction of sites with errors of less than 5% increased to 57% and 59% respectively.

TABLE 21. SUMMARY OF HIGH VOLUME FLOW RATE AUDITS

	Year 1 1977	Year 2 1978	Year 3 1979	Year 4 1980
Number of Agencies	15	16	26	26
Number of Sites	40	38	126	58
Calibration Error Range	Percentage of Sites			
0 - 5%	20	39.5	57.1	58.6
5 - 10%	37.5	55.3	28.6	19.0
10 - 15%	15	2.6	6.3	13.8
15 - 20%	20	2.6	3.2	1.7
20 - 25%	0	0	3.2	0
25 - 30%	0	0	1.6	0
> 30%	7.5	0	0	6.9

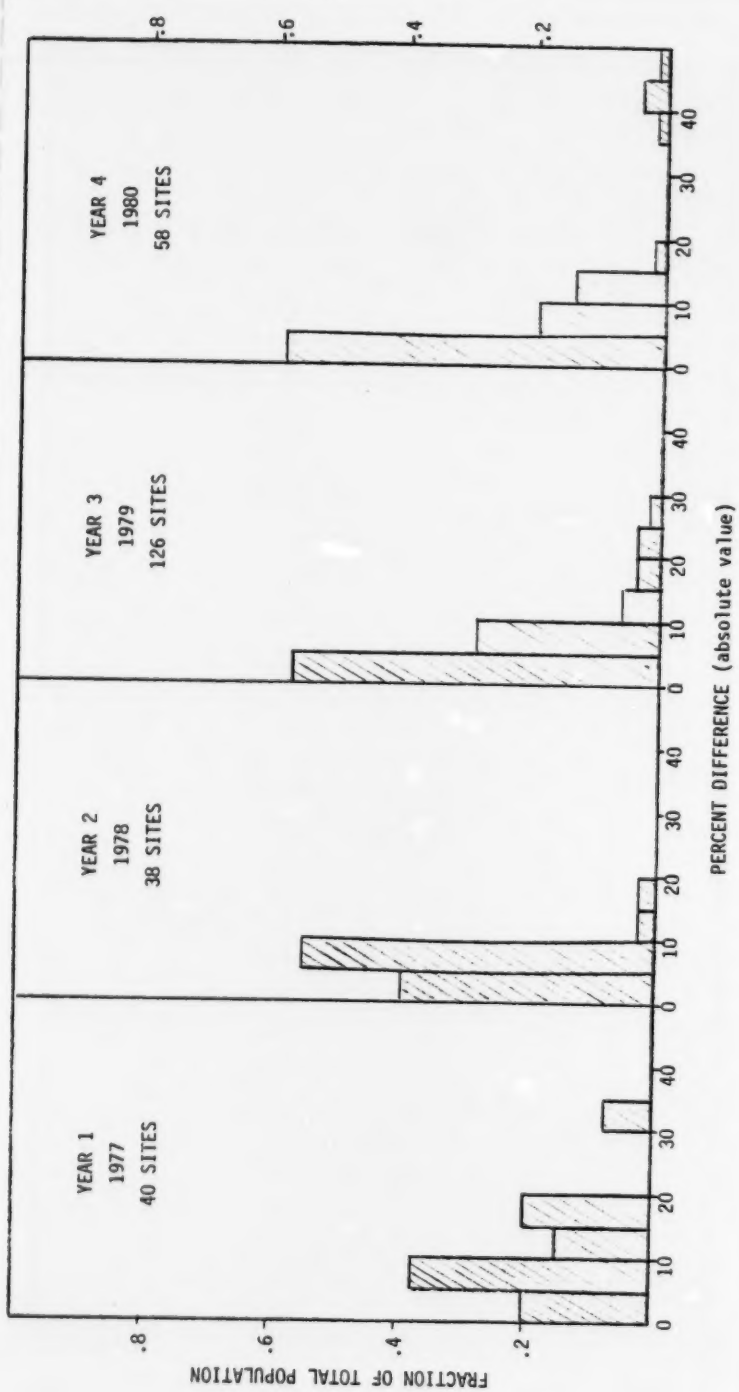

Figure 1. Histograms illustrating improvement in high-volume flow rate calibration performance.

SECTION 5

PERFORMANCE AUDITS

Performance audits of air monitoring stations operated by participating groups was a major task in the Western and Eastern QA programs. Table 22 to 26 show lists of all sites audited during the lifetime of the program. The total number of station audits is approximately 425. Individual reports for these audits have been issued and are on file with EPA in RTP. These reports should be consulted for detailed results and discussion. Generally each audit report refers to only one agency and describes the results obtained for several stations audited during one trip.

TABLE 22. SUMMARY OF AUDITS PERFORMED BY ROCKWELL IN 1976

		1976			
Agency	Site	S	O	N	D
Colorado Oil Shale Tract, C-a	1				✓
Colorado Oil Shale Tract, C-b	023				✓
State of Colorado	CARIH				✓
State of Montana	Colstrip	✓			
	Billings	✓			
	Laurel	✓			
National Oceanic and Atmospheric Administration (NOAA)	Boulder				✓
State of North Dakota	Stanton				✓
Utah Oil Shale Tracts, U-a/U-b	A6			✓	
State of Utah	Price			✓	
	Huntington			✓	
State of Wyoming	Patrick Draw			✓	

TABLE 23. SUMMARY OF AUDITS PERFORMED BY ROCKWELL IN 1977

Agency	Site	1977											
		J	F	M	A	M	J	J	A	S	O	N	D
Colorado Oil Shale Tract C-a	1				✓				✓			✓	
Colorado Oil Shale Trace C-b	023				✓				✓			✓	
State of Colorado	CARIH				✓			✓			✓		
	Greeley							✓			✓		
	Grand Junction											✓	
	Arvada							✓			✓		
	Welby										✓		
	Colorado Springs							✓			✓		
	CAMP							✓			✓		
EPA Quality Assurance Division (QAD)	RTP					✓			✓			✓	
EPA/Corvallis	Colstrip									✓			
State of Montana	Colstrip						✓			✓			
	Billings			✓			✓			✓			
	Laurel			✓			✓			✓			
	C-Hill						✓			✓			
	Highway Junction						✓			✓			
	Microwave						✓			✓			
	Saddle Mountain						✓			✓			
	Butte									✓			
State of New Mexico	Farmington		✓										
	Water Tank		✓										
	Substation		✓										✓
	Reservation		✓										✓

(Continued)

TABLE 23. (Continued)

Agency	Site	1977 J	F	M	A	M	J	J	A	S	O	N	D
NOAA	Boulder				✓			✓					
State of North Dakota	Stanton				✓					✓			
	Bismark									✓			
Utah Oil Shale Tracts, U-a/U-b)	A6				✓				✓				✓
State of Utah	Price				✓					✓			
	Huntington				✓		✓			✓			
	Salt Lake City						✓			✓			
	Magna						✓			✓			
	Bountiful						✓						
	Ogden						✓			✓			
	Provo						✓			✓			
	Cedar City #1											✓	
	#3											✓	
State of Wyoming	Patrick Draw				✓				✓				✓
Northrop Services, Inc. (NSI)	Las Vegas												✓
Lawrence Livermore Laboratory (LLL)	Imperial Valley #2			✓		✓							✓
	#3												✓
	#6												✓

TABLE 24. SUMMARY OF AUDITS PERFORMED BY ROCKWELL IN 1978

Agency	Site	1978											
		J	F	M	A	M	J	J	A	S	O	N	D
Colorado Oil Shale Tract, C-a	1			✓			✓			✓			✓
Colorado Oil Shale Tract, C-b	023			✓			✓			✓			✓
State of Colorado	CARIH		✓			✓			✓			✓	
	CAMP		✓			✓			✓			✓	
	Greeley		✓			✓			✓			✓	
	Arvada		✓			✓							
	Colorado Springs		✓			✓			✓			✓	
	Welby		✓			✓			✓			✓	
	Grand Junction			✓									
EPA/Custer, MT	Custer					✓							
EPA/QAD	RTP			✓		✓			✓				
Northrop Services, Inc.	Las Vegas				✓			✓		✓			✓
EPA/Corvallis	Hae Koolie	✓			✓			✓			✓		
	B&W							✓			✓		
Lawrence Livermore Laboratory	Imperial Valley #6				✓								
	Mobile				✓								
Air & Industrial Hygiene Laboratory (AIHL)	Berkeley		✓										

(Continued)

TABLE 24. (Continued)

Agency	Site	1978 J	F	M	A	M	J	J	A	S	O	N	D
State of Montana	Billings	✓			✓				✓		✓		
	Laurel				✓						✓		
	Highway Junction	✓			✓				✓		✓		
	Millcreek	✓											
	Broudy	✓			✓								
	Microwave	✓			✓								
	Hebgen				✓				✓		✓		
	Lions Park				✓				✓		✓		
	Alpine West	✓			✓								
	Lincoln School				✓				✓		✓		
	Manfunction Junction				✓								
State of New Mexico	Reservation			✓			✓			✓			✓
	Substation			✓			✓			✓			✓
	Water Tank			✓			✓			✓			✓
	State Calibrator						✓						
NOAA	Boulder					✓						✓	
State of North Dakota	Stanton	✓			✓			✓			✓		
	Bismarck	✓			✓			✓			✓		
Utah Oil Shale Tracts U-a/U-b	A6			✓			✓			✓			
State of Utah	Price	✓			✓			✓					
	Huntington	✓			✓			✓			✓		
	Bountiful	✓			✓			✓			✓		
	Provo	✓			✓			✓			✓		
	Magna	✓			✓			✓			✓		
	Ogden	✓			✓			✓			✓		

(Continued)

TABLE 24. (Continued)

Agency	Site	1978 J	F	M	A	M	J	J	A	S	O	N	D
State of Utah (Continued)	Cedar City #1						✓			✓			✓
	#2				✓		✓			✓			✓
	#3				✓								
	State Calibrator	✓			✓			✓			✓		
Woodward Clyde	Roosevelt Hot Springs						✓			✓			
State of Wyoming	Patrick Draw			✓			✓			✓			
City of Alexandria	Health Department											✓	
Farifax County	McLean											✓	
State of Virginia	ABC Warehouse											✓	
	VA School											✓	
	Norfolk Airport											✓	
Washington, DC	Laboratory											✓	
	Library											✓	

TABLE 25. SUMMARY OF AUDITS PERFORMED BY ROCKWELL IN 1979

Agency	Site	1979											
		J	F	M	A	M	J	J	A	S	O	N	D
Colorado Oil Shale Tracts, C-a	1			✓			✓			✓			✓
Colorado Oil Shale Tracts, C-b	023			✓			✓			✓			✓
State of Colorado	CARIH		✓				✓						
	CAMP		✓				✓			✓			✓
	Colorado Springs		✓				✓						
	Greeley		✓				✓						
	Welby		✓				✓						
EPA/QAD	RTP	✓				✓		✓			✓		
Northrop Services, Inc.	Las Vegas			✓			✓			✓			
EPA/Corvallis	Hae Koolie		✓						✓				
	Greenleaf								✓				
State of Montana	Billings Central Pk		✓			✓			✓			✓	
	Laurel					✓			✓			✓	
	Hebgen Park		✓			✓							
	Highway Junction		✓			✓							
	Gate		✓										
	Lincoln School		✓			✓							
	Lions Park		✓			✓							
	Lockwood School					✓			✓			✓	
State of New Mexico	Reservation			✓			✓			✓			✓
	Substation			✓			✓			✓			✓
	Water Tank			✓			✓			✓			✓

(Continued)

TABLE 25. (Continued)

Agency	Site	1979 J	F	M	A	M	J	J	A	S	O	N	D
State of New Mexico (Continued)	State Calibrator									✓			✓
	Office			✓			✓			✓			✓
NOAA	Boulder		✓				✓						
State of North Dakota	Stanton	✓				✓			✓				
	Dunn Center											✓	
Utah Oil Shale Tracts U-a/U-b	A6			✓			✓			✓			✓
State of Utah	Bountiful	✓			✓								
	Castle Dale	✓			✓		✓			✓			✓
	Cedar City #2			✓			✓			✓			✓
	Magna	✓			✓								
	Mills				✓		✓			✓			
	Vernal									✓			✓
	Ogden	✓			✓								
	Provo	✓			✓								
	Salt Lake City	✓			✓								
	State Calibrator	✓			✓								
North American Weather	Salt Lake City	✓											
State of Wyoming	Casper			✓		✓				✓			✓

(Continued)

TABLE 25. (Continued)

Agency	Site	1979 J	F	M	A	M	J	J	A	S	O	N	D
Eastern Groups													
Allegheny County	Hazelwood	✓											
	Downtown	✓											
City of Cincinnati	Ripple Road					✓							
	Sycamore					✓							
City of Baltimore	Read Street			✓									
County of Baltimore	Essex			✓									
Dayton/RAPCA	Springfield					✓							
	Northridge					✓							
	Mad River Trailer					✓							
	County Building					✓							
	Salem					✓							
State of Delaware	P-1		✓										
	P-2		✓										
State of Indiana	Hammond					✓							
	Indy					✓							
State of Maryland	Baltimore 01			✓									
	Baltimore 02			✓									
	Bethesda 06			✓									
	Suitland 05			✓									
Carrol County	LLL Trailer, Mt. Airy			✓									

(Continued)

TABLE 25. (Continued)

Agency	Site	1979 J	F	M	A	M	J	J	A	S	O	N	D
Ohio Edison	Adams				✓								
	P. Hills				✓								
	School				✓								
	Anserphone				✓								
Pennelec	Laboratory				✓								
	Parkwood				✓								
	Gas Center				✓								
State of Pennsylvania	Beaver Falls	✓											
	Baden	✓											
	Johnstown	✓											
	Harrisburg	✓											
City of Philadelphia	Laboratory		✓										
	Broad and Spruce		✓										
State of West Virginia	Charleston					✓							
	Wheeling					✓							
	Weirton					✓							
	Follosbee					✓							

TABLE 26. SUMMARY OF AUDITS PERFORMED BY ROCKWELL IN 1980

Agency	Site	1980											
		J	F	M	A	M	J	J	A	S	O	N	D
Colorado Oil Shale Tract, C-a	1			✓			✓		✓				
Colorado Oil Shale Tract, C-b	023			✓			✓		✓				
State of Colorado	CAMP		✓				✓		✓				
EPA/QAD	RTP	✓			✓								
State of Montana	Central Park		✓			✓							
	Lockwood		✓			✓							
	Laurel		✓			✓							
State of New Mexico	Reservation			✓			✓						
	Substation			✓			✓						
	Water Tank			✓			✓						
	Office			✓			✓						
State of North Dakota	Dunn Center		✓			✓							
Utah Oil Shale Tracts, U-a/U-b	A6			✓			✓						
State of Utah	Castledale							✓					
	Cedar City				✓		✓						
	Vernal			✓			✓		✓				
State of Wyoming	Casper		✓				✓		✓				

The audit procedure consisted of delivering to each analyzer five different concentrations of pollutant, including zero, using a portable audit device. The output of the analyzer was measured with a digital voltmeter or with the measuring device used in the station. The result of each audit is a five-point response curve which is graphed and compared with the latest calibration curve in use at the station. To distinguish between the audit curve and the station calibration curve, audit results are sometimes referred to as the "calibration audit." The constants derived from the audit curve were used by Rockwell, EPA, and the agency for evaluating the station calibration. The "calibration audit" was not intended to give a substitute calibration for use by the agency for data reduction. Where the differences between the station calibration and audit results were unusually large, attempts were made to locate the source of the problem.

In addition to the audit of the continuous analyzers, checks were also made on the high volume flow rate using calibrated orifice plates.

Detailed audit procedures as well as a description of the audit equipment and standards are given in Appendix A of this report. Appendix A also includes information about internal checks and procedure for certifying audit devices for reliability and accuracy.

EVALUATION CRITERIA

Each instrument audit provided a comparison between the station calibration curve and the audit calibration curve. The format for presenting the results underwent several changes during the course of the program. Prior to June 1978, audit results were given in terms of linear constants describing the response of the analyzer to known pollutant concentrations. The relationship was described by equations of the form $C = A + BX$, where C is the concentration in ppm, X is the analyzer output measured in some convenient form (mV, volts, % chart, chart division, etc.), and A and B are linear constants. Comparisons were made by calculating values of C at full scale from the station curve and the audit curve, and determining the percent difference between the two values. In this reporting format the magnitude of B depends on the units of X and therefore comparison of calibration constants among different instruments and agencies was difficult.

At the request of EPA a second method was adopted for reporting audit results, starting with audits performed after June 1978. The second method compares the concentrations delivered to the analyzer from the audit device to those predicted from the observed instrumental response and the latest station multipoint calibration. Mathematically, the results are expressed in the form $C_2 = \alpha + \beta C_1$, where C_2 is the station concentration, C_1 is the audit concentration, β is the slope, and α is the intercept. Perfect agreement between station and audit is represented by the "unity line" $\beta = 1$, $\alpha = 0$. Audit reports show graphs of C_2 vs C_1, and the values of α and β are given in tabular form. The advantage of the second method is that β is non-dimensional, and its value is independent of the analyzer range and the units used to express analyzer output.

The percent difference between station concentrations are readily expressed in terms of the magnitude of α and β by means of the equation:

$$\% \text{ diff} = 100 \times \frac{C_2 - C_1}{C_1} = 100 \left[(\beta - 1) + \frac{\alpha}{C_1} \right] .$$

In order to evaluate the station performance the percent difference is calculated at the nominal scale of the analyzer (for example: C_1 = 0.5 ppm for most NO analyzers). Since normally the magnitude of α/C_1 is small compared to β-1, the percent difference is approximately a constant represented by the quantity 100 (β-1). This latter relationship makes β a useful comparison parameter.

Although methods 1 and 2 appear to give different measures of comparison it can be easily shown that the two methods are in fact equivalent.

In May 1979, EPA published a set of quality assurance regulations under EPA 40 CFR Part 58, "Air Quality Surveillance and Data Reporting;" Appendix A - Quality Assurance Requirements for State and Local Air Monitoring Stations (SLAMS)[3]. The regulations describe still a third method for evaluating calibration performance. The regulation requires calculating the percent difference d_i for each specified audit concentration.

If two or more analyzers measuring the same pollutant are audited within one agency, the average $\bar{D}$ and the standard deviation Sa of the individual percent differences are calculated for each audit concentration level. $\bar{D}$ and Sa are used to estimate the upper and lower probability limits (measured as a percent) which comprise 95% of all the audit data and can be used to predict where future measurements are expected to be. Audit reports since August 1978 include tables of d_i, $\bar{D}$, and Sa, but no attempts have been made to interpret these data.

For the purposes of this program percent difference at full scale was used for the most convenient criterion for overall performance evaluation, since the intention was to assess improvements in the agencies' calibration accuracy, rather than to compute confidence intervals for estimating validity of air monitoring data.

Criteria for evaluating differences between station measurements and audit results were not rigidly defined or established by EPA. The definition of "satisfactory" or "unsatisfactory" accuracy is necessarily arbitrary and depends on the intended use of the data as defined by both agencies involved and the EPA.

For the purpose of the Rockwell audits, the following working guidelines were adopted:

Discrepancies of 10% or less at full scale required no specific corrective action and were considered "satisfactory."

Discrepancies in excess of 10% at full scale were of immediate concern. In such cases, Rockwell made a specific attempt to locate the source of

the problem and, if this was not practical, likely sources of error were identified and recommendations were made to the agencies for further study. A typical recommendation was for the agency to recalibrate the analyzer in question.

AUDIT RESULTS

During the four years of the program, over 420 station audits were performed; hence a very large amount of data has been collected. Twelve quarterly audits have been performed in the EPA Quality Assurance Division (EPA/QAD) laboratory at Research Triangle Park (RTP), NC for the purpose of comparing standards and procedures between Rockwell and EPA. The results of these special audits have been very satisfactory as the difference between the two laboratories have been generally 5% or less.

Table 27 and Figures 2 and 3 summarize overall performance in both tabular and graphical form for each type of pollutant. The table shows the total number of audits, the average percent error at full scale (calculated as described earlier in this section but without regard to the sign) and the percent of audits in which the error is equal or less than 5%, 10%, and 15%. The entries in Table 27 are arranged by program year (October 1 to September 30). Figures 2 and 3 show the average percent error at full scale for each type of pollutant plotted as a function of time. In these figures the data points are calculated by averaging over all the audits performed in each quarter, except that audits during the first two quarters of the program are combined and shown in quarter number 2.

Table 27 and Figures 2 and 3 present clear evidence of the impact of repeated QA audits on the quality of the data generated by the participating groups. The most remarkable improvement in calibration accuracy is noted for NO, NO_x, and NO_2. For example the average percent error for NO decreased steadily from 15.5% in the first year to 6.2% in the fourth year and also the fraction of audits in which the error was 10% or less increased from 59% in the first year to 83% in the fourth year. Similar results are observed for NO_x and NO_2. The overall performance for O_3 calibration has undergone significant improvement as the average percent error decreased from 13.5% in the first year to 7.0% in the fourth year. However, the change is not as pronounced as that for NO-NO_x, as evidenced in Figure 2.

For SO_2 a somewhat different pattern is observed. In the first year of the program the average percent error was about 16%, while in the remaining three years the average percent error remained nearly constant at 8-9%. Several groups displayed large calibration differences in the beginning of the program which were caused by procedural or calculation errors. After these large errors were discovered and eliminated, the performance has remained nearly constant, indicating that 8-9% is the best that can be expected for SO_2 using the current calibration methods.

The average percent error for CO has been less than 5% since the second quarter of the program. Also the percent of audits in which the error was 10% or less has been above 80% from the start of the program. This is excellent agreement and it clearly indicates that calibration of CO presents no difficul-

TABLE 27. SUMMARY OF AUDIT RESULTS

Year	No. of Audits	Ave. % Error	Percent Audits Error ≤5%	Percent Audits Error ≤10%	Percent Audits Error ≤15%
NO					
1	34	15.5	32	59	65
2	65	8.8	49	74	82
3	56	7.1	50	75	88
4	23	6.2	61	83	96
NO_x					
1	28	16.6	39	50	57
2	58	7.8	53	76	84
3	57	7.3	49	81	88
4	19	4.3	68	89	100
NO_2					
1	24	17.5	33	46	63
2	53	7.4	58	81	83
3	74	8.4	36	74	84
4	24	3.9	71	100	100
O_3					
1	36	13.6	28	64	72
2	90	10.8	38	54	72
3	101	9.5	41	61	77
4	29	7.0	62	76	83
SO_2					
1	64	15.8	36	58	66
2	100	8.8	42	72	84
3	128	8.2	45	74	84
4	46	9.6	37	72	83
CO					
1	23	8.2	17	83	96
2	57	4.7	63	88	98
3	68	4.3	65	96	100
4	22	4.0	73	100	100
CH_4/THC					
1	27	10.1	44	78	89
2	43	6.5	63	77	95
3	35	4.2	65	94	100
4	16	5.1	75	88	94

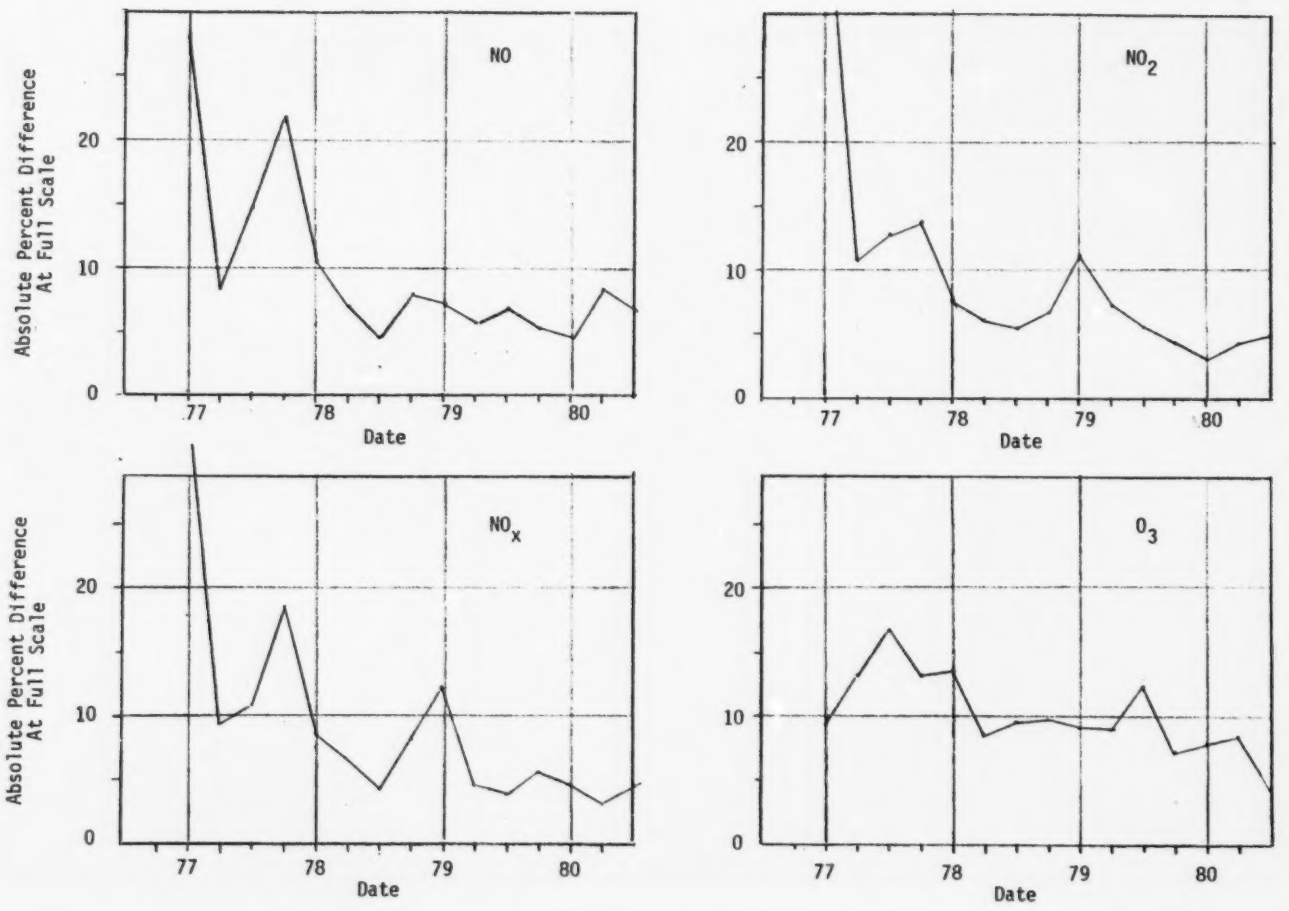

Figure 2. Average calibration error as a function of time for NO, NO_x, NO_2 and O_3.

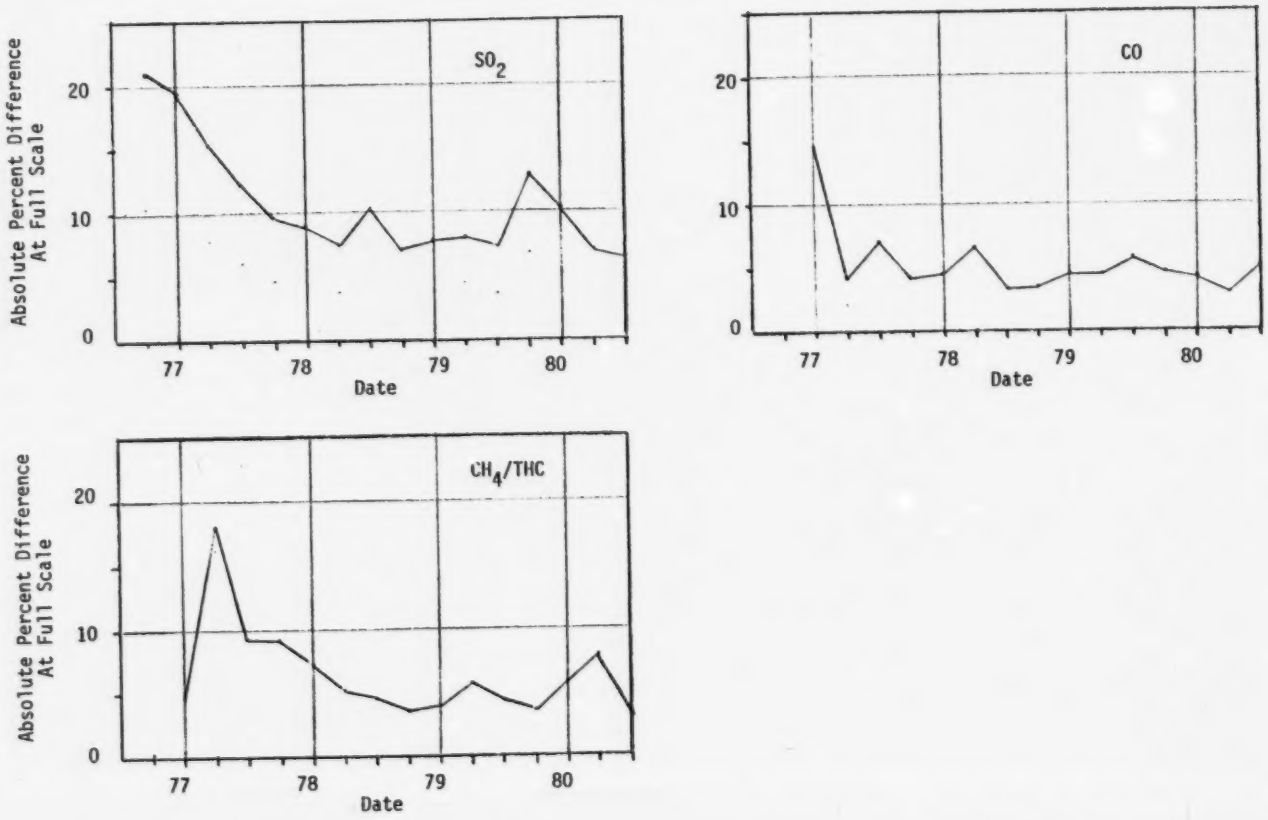

Figure 3. Average calibration error as a function of time for SO_2, CO, and CH_4/THC.

ties. This conclusion is consistent with the results of the interlaboratory CO performance audits described in Section 4.

The situation for CH_4/THC is somewhat comparable to that of SO_2 in that most of the observed improvement occurred after the first year of the program. In general the CH_4/THC results have been quite satisfactory in that the percentage of audits in which the error was 10% or less has been 77% or higher throughout the program.

SECTION 6

TECHNICAL ASSISTANCE

In accordance with the provisions of the contract, Rockwell has provided technical assistance to the various participating agencies as requested by the Project Officer. Some of the assistance has been relatively minor, and consisted of telephone discusssions of various agency problems, citing literature references or help with procedural difficulties.

Much technical assistance was given informally during site evaluations and particularly during field audit visits where the exchange of ideas and information between Rockwell and Agency personnel was oftentimes extensive.

The following sections summarize the various types of technical assistance provided by Rockwell to the participants of the program. In general technical assistance was requested by the monitoring organization and approved by the EPA QA regional coordinator as well as the EPA Project Officer.

TECHNICAL ASSISTANCE AREAS

Air Monitoring Procedure and Quality Assurance

Many agencies requested technical assistance in the general area of air monitoring. Rockwell in effect served for four years as consultant to the agencies and provided information, advice, and documents concerning monitoring techniques and procedure, equipment selection, quality assurance, specific calibration methods and standards. A common technical assistance request was for specific written instructions for calibrating ozone monitors by means of GPT and UV photometry. Other documents that were supplied to agencies were written procedures for flow rate calibrations of high volume samplers and dilution devices. While some documents were taken from EPA literature, many of the procedures were written by Rockwell personnel for use in the Rockwell laboratory.

Rockwell personnel visited an EPA regional laboratory early in the program in 1976 and provided assistance in procedures for modifying a trailer equipped with monitoring equipment.

One state agency shipped its calibration apparatus in May 1977 to the Rockwell laboratory for inspection and testing. The calibrator was found to be defective and in need of repair. Rockwell recommended that the equipment be sent to the manufacturer for complete overhaul.

At the request of the EPA Project Officer, a portable SO_2 audit device developed by Research Triangle Institute was tested in May 1979 in the Rockwell laboratory and subsequently used in field audits in New Mexico and Montana.

The Rockwell QA laboratory was a participant in a cooperative joint study conducted by EPA/RTP in September 1977 to evaluate and compare the BAKI procedure for calibration of ozone to the gas phase titration and UV absorption techniques.

A special study was conducted in February 1978 at the Rockwell QA laboratory to determine what effect the diluent gas (air or nitrogen) present in a hydrocarbon calibration standard has on the response of a flame ionization detector (FID). This work was necessary because of unexpected large differences observed in audits of a total hydrocarbon analyzer operated in one of the oil shale tracts. The study demonstrated that methane in nitrogen behaves differently from methane in air when injected in an FID gas chromatograph. It was concluded that methane in air should always be specified as a calibration standard for total hydrocarbon analyzers.

Chemical Analysis Quality Control and Procedure

Technical assistance was provided to several agencies on laboratory procedure and quality control techniques. Early in the program three agencies needed assistance in setting up their Technicon Analyzers. Written procedures used in the Rockwell laboratory for filter extraction and analysis of trace metals were sent to requesting agencies. Information was also sent on the use of quality control charts in routine laboratory analysis. Some agencies requested and received additional laboratory audit samples for use as training material for their laboratory personnel. The laboratory supervisor from one agency visited the Rockwell laboratory for several days on two separate occasions to discuss laboratory quality control, and the use of Atomic Absorption (AA) and Technicon analyzers. In addition Rockwell personnel spent a week in a state laboratory consulting on general laboratory procedure with special emphasis on the analysis of trace metals by the AA method. The Program Manager, together with a representative from an EPA regional office, also visited the headquarters of a state agency to discuss laboratory performance and problems which became apparent during the course of the QA program.

Split Sample Analysis of Trace Metals

An extensive split sample analysis program was carried out during 1977 and 1978 with a private laboratory performing analysis for EPA. The purpose of this program was to duplicate approximately 10% of the analysis performed by this laboratory for metals collected with particulates in high-volume filters. Initial sample analysis disclosed very large differences between laboratories. A test program was designed by Rockwell to investigate the source of the differences by using synthetic samples. The conclusion of the test was that differences in analysis could be ascribed to differences in extraction procedures. As a result of the interlaboratory study the private laboratory was directed by EPA to adopt the Rockwell procedure. Subsequent comparisons showed significant improvement in results for Cu, Fe, and Mn.

A similar split sample analysis program was also carried out with a state laboratory during the period between December 1977 and June 1978. Early analyses disclosed good agreement for Cd, Cu, and Pb, fair agreement for As, and poor agreement for Al, Fe, and Zn. The comparisons completed in June 1978 showed remarkable improvement in the analysis of Fe and Zn. The As comparison also showed improvement, possibly as a result of the implementation by the agency of a more precise automated flameless technique used by Rockwell. Differences in the Al analysis led to the discovery of a faulty nitrous oxide delivery system in the state's laboratory.

A split sample analysis program with a second state laboratory was initiated early in 1978. Initial comparisons disclosed very large differences between the laboratory results and Rockwell. This program, however was not carried out to completion because the state did not send additional samples for further study.

Traceability Service to NBS Standards

A traceability service was set up by the Rockwell Quality Assurance Laboratory to provide NBS traceable calibration standards to the participating groups. Cylinders or permeation tubes were purchased by the organizations and sent to Rockwell for analysis by comparison with NBS SRM standards or laboratory standards which were directly traceable to NBS primary standards. Approximately forty-five calibration standards were certified and returned to the requesting organizations. Rockwell, with EPA approval, supplied sets of Class S weights to two groups which had requested this. These weights were purchased with program funds.

Special Meetings

Two review meetings were held with representatives from EPA/RTP, the EPA regional offices, and the western participants of the Quality Assurance Program. The first meeting in April 1977 in Denver was a general program review. It was designed to acquaint all participants with the objectives and goals of the program and to discuss administrative and technical procedures. A second meeting at which most of the Region 8 state participants gathered together was an EPA sponsored workshop held in Denver in May 1979. During this meeting the newly proposed EPA quality assurance regulations for air monitoring (Appendix A and B) were described in detail by EPA representatives from RTP. The Rockwell Program Manager presented a tutorial session on ozone calibration by the UV absorption technique.

Organizational meetings were held in June 1978 in Philadelphia and in September 1978 in Chicago with the eastern participants in Regions III and V to discuss in detail the scope of work of the quality assurance program. The purpose of these meetings was to initiate the activities extending the program to the eastern participants.

Special Audits

At the request of the EPA Project Officer, Rockwell provided a considerable amount of technical assistance to a number of agencies and groups by

carrying out specialized audits not otherwise scheduled in the program.

Several routine audits which were performed in a western field station resulted in large differences in the calibration of an SO_2 analyzer. A representative from the monitoring group visited the Rockwell QA laboratory in August 1977 and in conjunction with Rockwell personnel carried out a side-by-side calibration test using calibration equipment used by the two organizations. The test demonstrated that all the calibration equipment was in good order. However Rockwell discovered that the monitoring group was unknowingly committing a procedural error in the calculation wich resulted in a systematic error in the reported SO_2 concentration. The error effectively explained the previously observed differences.

A representative from another organization visited the Rockwell QA laboratory in July 1979 to compare calibration procedures and to perform an audit of the NO-NO_x analyzer using the organization's calibration equipment. The test uncovered a significant difference between the calibration procedures used by the two groups. However the test results indicated good agreement between laboratories.

A special audit of NO-NO_x and O_3 analyzers operated by the Air & Industrial Hygiene Laboratory (AIHL) in Berkeley, California was performed in February 1978 to try to determmine the cause for the large discrepancies observed in an air monitoring program conducted by another agency using NO standards provided by AIHL. The results remained inconclusive as far as the field work was concerned since the audit data at Berkeley showed excellent agreement.

Several one-time-only performance audits of air monitoring stations or equipment were carried out at various times at the request of a state agency or the Project Officer. The audits involved the following organizations and sites.

- EPA site, Custer National Forest; Custer, Montana, May 1978;
- Woodward Clyde Consultants; Roosevelt Hot Springs, Utah, June, 1978;
- North American Weather Consultants and State of Utah, Salt Lake City, Utah, January 1979;
- Anaconda Copper Co. and State of Montana; Anaconda, Montana, February 1979;
- Dichotomous Samplers operated for EPA by the State of Colorado; Denver, Colorado, February 1974;
- Lawrence Livermore Trailer; Mount Airy, Maryland, April 1979.

A complete system audit of the air monitoring activities by Kennecott Copper in the Salt Lake City area was carried out in April 1980 at the request of Region VIII. No performance audits were done under this program at the Kennecott site.

Guideline Reviews and Publications

At the request of the Project Officer and other personnel from EMSL/RTP several draft reports, guideline proposals, and technical assistance documents were reviewed and the comments submitted to the requesting individual. Some of the documents reviewed are listed below:

- Technical Assistance Document on the Use of the Flame Photometric Detector for the Measurement of SO_2.
- Criteria, Procedures and Forms for the Evaluation of Ambient Air Monitoring Programs (Section 2.0.11 of Volume II of the EPA Quality Assurance Handbook). (5)
- Specific Guidance for a Quality Control Program for SLAMS and PSD Automated Analyzers and Manual Methods (Section 2.0.9 of Volume II of the EPA Quality Assurance Handbook). (5)

A paper co-authored by M. Cher and E. P. Parry of Rockwell and S. Bromberg of EPA titled "Quality Assurance in Support of Energy Related Monitoring Activities" was presented at the Joint APCA/ASQC Conference on Quality Assurance in Environmental Measurements in New Orleans on March 1979. The paper, which describes objectives and activities of the quality assurance program, was subsequently published in the Proceedings of the Conference.

A brief description of the quality assurance program was presented in a paper delivered by M. Cher at the Geothermal Environmental Seminar-'78 held in May 1978 in Sacramento, California.

REFERENCES

1. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I, Principles, EPA-600/9-76-005, March 1976.

2. Ambient Air Quality Surveillance, 40 CFR Part 58, Federal Register, Volume 44, No. 92, May 10, 1979, p. 27571.

3. AppendiX A, Quality Assurance Requirements for State and Local Air Monitoring Stations (SLAMS), Federal Register, Volume 44, No. 92, March 10, 1979, p. 27574.

4. National Primary and Secondary Ambient Air Standards, Appendix B, Federal Register, Volume 36, No. 84, Part II, April 30, 1971.

5. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Ambient Air Specific Methods, EPA-600/4-77-027a, May 1977.

APPENDIX A

DESCRIPTION OF AUDIT PROCEDURES AND EVALUATION CRITERIA

A description of the apparatus, calibration standards, audit procedures, data analysis, and evaluation criteria is presented in this Appendix.

APPARATUS AND CALIBRATION STANDARDS

The Rockwell portable audit device was designed and built by Rockwell at the EMSC. It is used in the audits of all continuous monitors and is capable of generating and delivering mixtures of various gaseous pollutants in air at precisely known concentrations. Mixtures are produced in one of four ways:

1. By dilution of gases contained in cylinders at high concentrations (e.g., NO, CO, CH_4).

2. By gas phase titration (e.g., NO_2).

3. By dilution of ozone produced by an ozone generator.

4. By dilution of gases diffusing from permeation tubes (e.g., SO_2).

The audit device contains two Tylan mass flow controllers to control and measure the flow of dilution air from the zero air source and span gas from the high concentration cylinders. The span gas flow controller has a range of either 0-50 or 0-30 cc/min. The dilution air flow controller has a range of either 0-10,000 or 0-15,000 cc/min. Flows are reproducible and accurate to $\pm$ 1%. Each flow controller is calibrated before and after each trip. Thus dilution factors between 15000/5 = 3000 and 1500/50 = 30 with an accuracy of $\pm$ 2% are readily attainable simply by adjusting two potentiometers for the desired flow. Since these flow controllers regulate and measure mass flow, the flow is independent of ambient temperature and pressure and it is given in standard cc/min (298°K/760 mm Hg).

Air flows through the permeation tube holders and the ozone generator constitute less than 10% of the total dilution flow. These flows are added as needed to the dilution flows, and hence they are controlled and measured with sufficient accuracy using needle valves and rotometers. A separate mass flowmeter is used to calibrate the rotometer scales.

The air oven in the audit device can be regulated to maintain a temperature of 30.0 $\pm$ 0.1°C. Contained in the oven are two permeation tube holders made from a solid Teflon block and three copper coils used to thermally

equilibrate the air flow streams before they enter the permeation tube holders and the ozone generator. The latter dissipates some heat, and thus it is kept in a separate temperature insulated enclosure outside the air oven.

The temperature of the oven is measured with two thermistor probes located in the air streams at the air inlet of the permeation tube holders. In this way temperature is measured as close as possible to the permeation tubes, without having the sensors come in direct contact with the SO_2 streams. The stability of sensor calibration is optimized by placing the entire measuring circuitry in the oven. A mercury-in-glass thermometer can also be placed in the center of the oven as an additional temperature check. Both the thermometer and the thermistor sensors are calibrated against an NBS standard thermometer.

Span gases passing through the flow controller are in contact with stainless steel, Teflon and glass. Ozone, sulfur dioxide and diluted gas streams are in contact with only Teflon or glass.

Zero Air

Zero air is generated from ambient air by means of a Rockwell-built, portable zero air source. Ambient air from the compressor is dried, ozonized, and passed through activated charcoal and particulate filters. The air can also be passed through a catalytic oxidizer. This zero air source then delivers air which is free of NO, NO_2, O_3, SO_2, CO and hydrocarbons at a flow and pressure which meet the requirements of the dilution air flow controller used in the portable audit device. The quality of the zero air has been tested at the Rockwell QA laboratory, and meets the standards required for field audits.

Nitric Oxide (NO)

The NO standards are cylinders containing approximately 100 ppm NO in nitrogen. The cylinders are analyzed at the EMSC by direct one-to-one comparison with a Standard Reference Material (SRM) cylinder obtained from the National Bureau of Standards (NBS) or an NBS-traceable secondary standard. The NBS standard,secondary standard, and cylinder under calibration all contain approximately equal concentrations of NO. The analysis is done with a dilution system and a NO-NO_x analyzer, using identical flows to eliminate flow measurement errors. The NO cylinders are also analyzed periodically for NO_2 by the Saltzman method to insure that the NO_2 content is less than 0.5% of the NO content.

Nitrogen Dioxide (NO_2)

NO_2 is generated during the gas phase titration of NO with ozone. The concentration of NO_2 is determined with a previously calibrated NO analyzer (using the NO standard) by measuring the decrease in NO concentration as ozone is added to the NO flow.

The converter efficiency of the NO-NO_x analyzer is audited during the gas phase titration procedure. The converter efficiency (CE) is calculated by

means of equation A-1:

$$CE = 100 \times \left[1 - \left(\frac{\Delta C_{NO_x}}{\Delta C_{NO}}\right)\right] \qquad (A\text{-}1)$$

where ΔC_{NO} and ΔC_{NO_x} are the changes (decreases) in concentrations of NO and NO_x which are observed during the titration. In calculating ΔC_{NO} and ΔC_{NO_x} due allowance is made for the dilution effect of the added ozone stream. If there is no change in the NO_x concentration, then the CE is 100%. If the value of CE is below 90% the converter is probably in need of repair. The above equation is used in preference to those published by the EPA in the Federal Register 41, December 1, 1976, pp 52686-52692. The EPA and Rockwell methods are equivalent.

Ozone (O_3)

The primary calibration standard for ozone is the known extinction coefficient of ozone at 254 nm, as used in the UV photometry technique described on Page 64. The gas phase titration procedure for NO_2 also calibrates the ozonze lamp in the audit device under ambient conditions at the site. Thus the calibrated ozone lamp could be used to audit the O_3 analyzer simply by turning off the NO flow. The latter procedure has been used extensively in the past, and may serve as a back-up procedure if the portable Dasibi monitor, used as UV transfer standard, is found to be malfunctioning.

Carbon Monoxide (CO)

The CO standards are cylinders containing 1000-5000 ppm CO in nitrogen or air. Cylinders are analyzed at the EMSC by comparison with either an SRM cylinder obtained from NBS or with an NBS-traceable secondary standard. The method is equivalent to the NO method described above except that a Bendix NDIR CO analyzer is used. Dilution flow corrections are made as necessary.

Hydrocarbons

These standards are cylinders containing approximately 1000 ppm methane or propane in air. Cylinders are analyzed at the EMSC by comparison with NBS or NBS-traceable cylinders. The method of analysis is essentially equivalent to that for CO but is performed using an FID gas chromatograph. Gas samples are injected undiluted and peak heights are used to calculate concentration.

Sulfur Dioxide (SO_2)

SO_2 standards are permeation tube devices. Normally, SO_2 permeation tubes are two or five centimeter SRM tubes obtained from NBS.[2] Since the supply from NBS is limited, tubes are also obtained from Metronics Corporation and these are calibrated gravimetrically. During the audit tubes are maintained at 30.o° $\pm$ 0.1°C in the portable audit device's oven. Occasionally when auditing an analyzer which requires an unusually high sample flow, an aluminum cylinder containing approximately 100 ppm SO_2 in air is used as the

SO_2 standard. The concentration of the SO_2 is determined by dilution using an SO_2 analyzer calibrated against an NBS permeation tube standard.

Laboratory Check of the Portable Audit Device

The portable audit device is checked at the EMSC before and after each audit trip. The test includes a multipoint flow calibration check of the two flow controllers to assure that the flows have not changed by more than 1%. A full performance test is then accomplished as described in the following paragraphs.

An analyzer is first calibrated at a single point to determine its sensitivity (in ppm/volt). For this purpose a fixed laboratory calibrator is used. The analyzer is then calibrated again using the portable audit device. The analyzer sensitivity obtained with the portable audit device is compared to that obtained with the fixed calibrator. Ideally, the ratio should be 1.00. Sensitivity checks are made for NO, NO_x, NO_2, O_3 and SO_2, thus checking all functional components of the audit device. Since the object of the check is to evaluate the performance of the audit device, the same NO gas cylinder and SO_2 permeation tubes are used with both the fixed and portable audit calibration devices.

The fixed laboratory calibrator is intended to be the primary calibration source (except for O_3). It is functionally similar to the portable audit device, except that it is permanently attached to a laboratory bench and its major use is for checking the portable device. Since the laboratory calibrator is not designed for field use, the mixing chambers and connecting tubing are constructed of Pyrex glass using a minimum of demountable joints, and Pyrex and Teflon manual stopcocks. To attain precise temperature control, permeation tube holders are immersed in a constant temperature water bath rather than in an air oven.

Since two independently calibrated flow controllers are part of each device, the maximum difference between the two sensitivity determinations is 4%. The portable audit device is judged to be in good order if the ratio of sensitivities determined by using the two devices (i.e., the portable audit device and the fixed calibrator) is between 0.96 and1.04. A leak in the system, contaminated lines, bad flowmeter calibration, or other major problem would cause the experimentally determined sensitivity ratio to deviate significantly from 1.00, and corrective action would then be taken.

Table A-1 shows results of a typical audit device operational check performed immediately before and after an audit. Sensitivities are given in ppm/volt. Because the laboratory analyzers are used for laboratory testing and not for monitoring purposes, they are not maintained in calibration. Occasionally different analyzers are used in the before and after checkouts. Thus the constancy of the ratio of sensitivities before and after the audit should be evaluated rather than any constancy in the sensitivities themselves.

TABLE A-1 CALIBRATOR OPERATIONAL CHECK*
(Sensitivity in ppm/volt)

	8/13/80 (before audit)			9/9/80 (after audit)		
Channel	Portable P	Fixed F	Ratio P/F	Portable P	Fixed F	Ratio P/F
SO_2	5.088	5.230	0.973	5.603	5.484	1.022
NO	0.513	0.531	0.966	0.512	0.504	1.016
NO_2	0.550	0.558	0.986	0.467	0.457	1.022
O_3	0.485	0.481	1.008	0.535	0.526	1.017

* Audit device No. 1, colloquially known as Bessie.

Laboratory Check and Calibration of the Ozone Transfer Standard

The calibration procedure for ozone is based on the UV photometry principle, as prescribed by EPA in the Federal Register, Volume 44, No. 28, Thursday, February 8, 1979.

The ozone transfer standard is an unmodified Dasibi ozone monitor. The calibration procedure is to measure the output of an ozone generator simultaneously using the transfer standard and the laboratory's UV photometer. This measurement is repeated at several concentrations (including zero) in order to obtain a linear correlation in the form $C_1 = A+BC_2$, where C_1 is the "true" O_3 concentration given by the UV photometer, C_2 is the indicated concentration of the transfer standard, and A and B are empirically determined linear regression constants. For field audits the above linear equation is applied to the field measured C_2 in order to determine the "true" ozone concentration.

The laboratory UV photometer is a modified Dasibi monitor. It differs from the standard Dasibi ozone monitor in that the internal scrubber is removed, and in its place zero air is plumbed directly to the instrument. The same air source that supplies zero air to the photometer also supplies air to the ozone generator. The UV photometer is kept in the laboratory and its sole function is to calibrate transfer standards.

The indicated output of the Dasibi monitor (including the UV photometer) is related to ozone concentration in ppm, but the magnitude of the indication depends on temperature, pressure, the fraction of ozone lost at the walls of the photometer cell, and the manually selected span value. The relationship is as shown in equation (A2):

$$[O_3]_{out} \text{ in ppm} = (\text{Dasibi Reading}) \left[\frac{10^6}{\alpha \ell I_o L} \quad \frac{T}{273} \quad \frac{760}{P} \right] \qquad \text{(A-2)}$$

where:

$[O_3]_{out}$ = concentration of ozone in ppm

α = extinction coefficient at 254 nm = 308 $Atm^{-1}Cm^{-1}$ at 0°C, 760 mn Hg

ℓ = optical path length = 71 cm (fixed by the Dasibi geometry)

T = cell temperature in °K (typically 10-12° higher than room temperature)

P = ambient barometric pressure in mm Hg

I_o = manually selected span value

L = correction factor for O_3 losses = (1 - fraction of O_3 lost).

To make the Dasibi reading be numerically equal to the ozone ppm, the value of I_o is chosen to make the quantity in brackets exactly unity. In an air-conditioned site T is approximately 310°K and P depends on the altitude. Thus I_o is site dependent and the appropriate value must be calculated from the measured P, T and L as described above. The quanity L is determined for the photometer and for each analyzer by measuring the ozone concentration at the output manifold as well as near the inlet and outlet of the photometer cell. An auxiliary ozone anayzer which has been calibrated assuming no wall losses is used for this purpose. The value of L is determined in the laboratory at approximately monthly intervals. If L is below 0.95, the photometer cell must be opened and cleaned.

AUDIT PROCEDURE

The audit procedure consists of delivering to each analyzer five different concentrations of pollutant, including zero ppm, using the portable audit device. Audit concentrations are calculated from the known concentration of the standard cylinders or the permeation rate of the permeation tubes, and the measured flows. For the ozone audit, the audit concentrations are determined by means of the transfer standard. The output of the station analyzer is read from the measuring instrument normally in use by the station. This readout device is either a recorder, a data-logger, a mini-computer, or a voltmeter, and the output parameter is either chart divisions, percent deflection, digital voltage, or ppm concentration. The results of the audit is in effect a five-point calibration which is compared with the latest station calibration by one or more methods, as described below. When differences between Rockwell and the Agency ppm values are large, an attempt is made to locate the source of the problem.

Depending on the full-scale operating range of the analyzer, audit concentrations will be chosen, if possible, to be within the concentrations specified in the following table.

Audit Point	Full-Scale Operating Range, ppm			
	0.5	1.0	50	100
1	0	0	0	0
2	0.03-0.08	0.03-0.08	3-8	3-8
3	0.15-0.20	0.15-0.20	15-20	15-20
4	0.28-0.33	0.40-0.45	28-33	40-45
5	0.40-0.45	0.80-0.90	40-45	80-90

If an analyzer is operated in a range different from those listed in the table, the audit concentrations will be selected approximately evenly over the operating range.

DATA ANALYSIS

There are at least two ways in which audit results and station calibration data can be treated to obtain a useful measure of agreement between the two. The first method is generally described in 40 CFR Part 58 - Ambient Air Quality Surveillance, and specifically in Appendix A - Quality Assurance Requirements for State and Local Air Monitoring Stations (SLAMS). These documents appeared in the Federal Register, Volume 44, No. 92, on Thursday, May 10, 1979, pp 27588-27604. The procedure is to calculate percent differences between the concentrations delivered to the analyzer from the portable audit device and those predicted from the latest station calibration. Details of the calculations are as follows.

Let C_1 represent the known concentration in the audit gas for the i^{th} audit point, and C_2 represent the concentration measured by the station. The percentage difference (d_i) is calculated using Equation A-3.

$$d_i = \frac{C_2 - C_1}{C_1} \times 100 \qquad \text{(A-3)}$$

Values of d_i are reported separately for each of the audit concentrations. For the zero ppm audit point the percent difference cannot be calculated and hence it is omitted.

If more than one analyzer measuring a given pollutant is audited, the average D and standard deviation Sa of the individual percent differences d_i are calculated for each audit concentration level according to Equations A-4 and A-5:

$$D = \frac{1}{k} \sum_{i=1}^{k} d_i, \qquad \text{(A-4)}$$

$$Sa = \sqrt{\frac{1}{k-1}\left[\sum_{i=1}^{k} d_i^2 - \frac{1}{k}\left(\sum_{i=1}^{k} d_i\right)^2\right]}, \qquad \text{(A-5)}$$

where k is the number of analyzers audited.

If only one analyzer measuring a given pollutant is audited, D and Sa are not evaluated. For these cases, the results of two consecutive audits are combined to obtain values for D and Sa according to Equations A-4 and A-5.

For each pollutant the 95 percent Probability Limits for the accuracy of a reporting organization at each audit concentration level are calculated using Equations A-6 and A-7:

$$\text{Upper 95 Percent Probability Limit} = D + 1.96\ Sa \qquad \text{(A-6)}$$

$$\text{Lower 95 Percent Probability Limit} = D - 1.96\ Sa. \qquad \text{(A-7)}$$

The second method of analysis of audit results involves the graphing of the station concentration (y-axis) versus the audit concentration (x-axis) for each of the pollutants audited. A table of the slopes and intercepts for each of these graphs is then prepared. Mathematically, the results are expressed by Equation A-8:

$$C_2 = \alpha + \beta C_1 \ , \qquad \text{(A-8)}$$

where C_2 is the station concentration, C_1 is the audit concentration, β is the slope, and α is the intercept. Perfect agreement between station and audit is represented on each graph by the dotted "unity" line ($\beta = 1$, $\alpha = 0$). A major advantage of this method is that β is non-dimensional and its value is independent of the analyzer range and the units used to express analyzer output. The magnitude of β is also a useful measure of relative agreement between station calibration and the audit results, as discussed below and the results of different audits for different agencies can be easily compared. Of course, details of station calibration, such as information about analyzer linearity, are lost.

The percent difference between station and audit concentrations can be readily expressed in terms of the magnitude of α and β, as shown in Equation A-9.

$$\%\ \text{Difference} = 100 \times \left[\frac{C_2 - C_1}{C_1} \right] = 100 \times \left[(\beta - 1) + \frac{\alpha}{C_1} \right] \qquad \text{(A-9)}$$

Since percent difference depends explicitly on the magnitude of C_i, it is convenient to choose C_1 equal to the operating full scale of the analyzer. The magnitude of α/C_1 is usually much smaller than $(\beta-1)$. It is this relationship which makes β a useful comparison parameter. There are two cases; however, where the percent difference is not determined primarily by the value of β. One case is where the intercept α is large; another case is where C_1 is very small. For these two cases, the percent difference is not a constant but depends on concentration. In order to give a more complete picture of the agency performance, audit reports show values of α and β for the latest audit, as well as a summary of the current and all previous values of β.

Field Audits of High Volume Samplers

A field audit of the high volume sampler consists of a single-point check of the flow rate in use during sample collection. The high volume sampler flow rate is measured by Rockwell using a calibrated orifice plate (Sierra Instruments) and a water manometer. The ambient temperature and pressure at the time of the audit are also measured using a pressure transducer and an NBS-traceable thermometer. At the same time that Rockwell determines the flow rate by measuring the pressure drop across the orifice, the agency determines the same flow according to its normal calibrating procedures.

Since there is as yet little uniformity among agencies in the way high volume flow is reported, the comparison between the audit measurement and the station calibration is made at the flow conditions specified by the agency. Typically, flow rates are reported at one of the following conditions:

(a) EPA Standard (298°K/760 mm Hg)

(b) Ambient temperature and pressure at time of audit

(c) Ambient conditions at time of last agency calibration

(d) Unspecified (this occurs, for example, if the agency uses a fixed chart to convert from sensor reading to flow rate without any corrections for temperature or pressure).

The mathematics used to calculate Rockwell's audit flow at the desired flow conditions are outlined below.

The flow rate through the orifice plate is initially calibrated in the Rockwell laboratory using a 5M 125 CTR Hi-Vol calibration meter (Rootsmeter). The flow rate is given by Equation A-10:

$$Q_{theo} = A + B\sqrt{\Delta P}\ , \qquad \text{(A-10)}$$

where Q_{theo} is the theoretical flow in cubic meters per minute (cmm) calculated for a measured pressure drop, ΔP, if the conditions during measurement were 760 mm Hg, 298°K. The constants A and B are empirically determined linear regression coefficients. Q_{theo} was obtained from the actual flow Q_1, measured with the Rootsmeter by means of Equation A-11:

$$Q_{theo} = Q_1 \left[\frac{P_1}{T_1}\ \frac{298}{760}\right]^{\frac{1}{2}} \qquad \text{(A-11)}$$

where P_1 is the barometric pressure and T_1 is the ambient temperature in the laboratory at the time of the orifice calibration.

During the field measurements, the audit value of Q_{theo} is obtained from the measured ΔP and Equation A-10. Q_{theo} is then converted to the appropriate agency reporting conditions using either Equations A-12 or A-13:

$$Q_2 = Q_{STD}\left(\frac{760}{298}\right)\left(\frac{T_2}{P_2}\right) = Q_{theo}\left[\frac{760}{298}\ \frac{T_2}{P_2}\right]^{\frac{1}{2}} \qquad \text{(A-12)}$$

$$Q_{STD} = Q_{theo}\left[\frac{P_2}{T_2}\ \frac{298}{760}\right]^{\frac{1}{2}} \qquad \text{(A-13)}$$

In Equation A-12 and A-13, Q_2 is the actual flow measured at ambient barometric pressure (P_2) and ambient temperature (T_2). Q_{STD} is the same flow corrected to the standard conditions of 760 mm Hg, 298°K. (Note $Q_{STD} \neq Q_{theo}$ unless $P_2 = 760$, $T_2 = 298$°K.)

The percent difference between the audit flow value and the agency flow value can then be calculated as a measure of agreement using Equation A-14:

$$\% \text{ Difference} = \frac{(\text{Agency Flow}) - (\text{Audit Flow})}{(\text{Audit Flow})} \times 100 \qquad \text{(A-14)}$$

EVALUATION CRITERIA

Each instrument audit results in a comparison betweeen the station calibration and the audit results. Usually the difference in the zero concentration output measured during station calibration and during the audit is negligibly small, and differences between the station calibration and audit results cause the graph of C_2 versus C_1 to have a slope different from unity. In such cases, the value of 100 (β-1) gives the percent difference between the station and audit concentrations for all values of C_1.

Criteria for evaluating differences between station and audit concentrations are not rigidly defined and have yet to be rigorously established. Any such criteria are necessarily arbitrary and depend on the intended use of the data.

For field audits, the following are offered as working guidelines. These are subject to revision and/or refinement:

Differences of 10% or less require no specific corrective action, and may be considered satisfactory.

Differences greater than 10% are of concern. Rockwell will make a specific attempt to isolate the source of the problem. Likely sources of error will be identified and recommendations will be offerred.

In addition to the percent differences mentioned above, Rockwell will discuss in the text of the report any deviations from "normal" ambient operation encountered during the audit. Examples are non-linear analyzer response, and low NO_2 converter efficiency. Again, specific corrective action may be recommended.